LOW TEMPERATURE CARBONISATION OF BITUMINOUS COAL

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LOW TEMPERATURE CARBONISATION OF BITUMINOUS COAL

BY

ANDREW McCULLOCH, A.I.C., A.M.C.T.

AND

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WITH NUMEROUS PHOTOGRAPHIC ILLUSTRATIONS AND DIAGRAMS

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PREFACE

The constant pollution of the atmosphere with smoke is an evil which is tardily recognised by the average citizen, and the damage and waste occasioned annually by the industrial and domestic consumption of raw coal is, perhaps, difficult to appreciate fully.

This evil may be considerably alleviated by the adoption of more efficient appliances, by the scientific control of existing plant, and by the more strenuous efforts on the part of smoke abatement organisations and municipal and national authorities.

The provision of a suitable smokeless fuel at a cost comparable with that of coal is, however, the only way in which a complete solution of the smoke evil can be attained in the near future.

By the carbonisation of coal at low temperatures, a solid smokeless fuel, together with fuel oil as the principal by-product can be produced from raw coal. The evolution of a system of low temperature carbonisation which can be successfully applied on a commercial scale is, therefore, of national importance. Not only will it be possible to ensure a smokeless atmosphere, but, at the same time, a considerable conservation of our coal resources will result, and the country will be provided with a home supply of fuel oil.

Much research work has been carried out and considerable private and public money expended in endeavouring to establish such a system of carbonisation. Whilst complete success has not been attained, great progress has been made within recent years, and developments are rapidly taking place.

In this book the authors have endeavoured to give a concise account of such progress, and of the difficulties yet to be surmounted.

Whilst it has been impossible in so small a work to do full justice to such an important subject, an attempt has been made to make it of general interest and of assistance both to technologists and to all concerned with the coal industries, and smoke abatement. Criticism whereby this object may be more nearly attained will be gladly welcomed.

In the course of compilation the authors have received every encouragement and help from fellow technologists and from others engaged industrially. In particular the fullest acknowledgment is due to the following gentlemen: Sir George Beilby, J. D. Davis, Wm. Everard Davies, E. C. Evans, N. H. Freeman, C. A. Grenfell, A. Grounds, F. D. Marshall, L. L. Summers, C. Turner and W. B. Smith.

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In conclusion the authors' thanks are due to F. S. Sinnatt for the interest he has shown in the work, and to Miss H. Greenleaves for the great assistance which she has given in the preparation of the manuscript.

Andrew McCulloch
Neville Simpkin

Manchester, 1923

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CHAPTER I

INTRODUCTION

INTRODUCTORY—COAL RESERVES—COAL CONSUMPTION IN GREAT BRITAIN—ECONOMIC USE OF COAL—WASTE OF RAW COAL—DOMESTIC FUEL AND THE LOSS OF BY-PRODUCTS—THE SMOKE PROBLEM—LEGISLATION—POLLUTION OF THE ATMOSPHERE—COMPOSITION OF SOOT—DAMAGE TO VEGETATION AND STRUCTURES—EFFECT OF SMOKE ON HEALTH.

The discovery of coal, and the recognition of its utility, together with the enormous advantages which it possesses over wood charcoal, have made our present day civilisation possible, and mark the definite transition period in the evolution of the agricultural England of the eighteenth century to the industrial England of the present day. The rich endowment of the coal fields to Great Britain has largely assured our position to-day as a leading nation, for upon the energy stored up within them, and upon the proximity of such potential energy to the other mineral wealth of the country, depends our capacity to transmute, produce, and move the materials on which everyday life exists.

The recognition of this fact places upon the present generation the onus and responsibility of enquiring how best we can utilise and conserve the coal yet stored up for future use, and direct the present line of inventive genius and thought to the discovery and development of other sources of power.

It has been estimated (International Geological Congress, 1913) that the total probable and possible coal reserves (all types) in the world within 600 ft. of the earth's surface are equal to 7,397,553 million metric tons, of which Great Britain possess 2·6 per cent. or 1/40, whilst that within the British Empire amounts to only about a quarter of these total reserves.

Estimates of the coal available in Great Britain within 4,000 ft. of the surface of the earth, making due allowances for the coal which must be left in the earth for surface support, pit wastage (allowing 15 per cent.), and the coal lying in seams too thin to be worked, have been made by recent authorities, and it is agreed to be in the region of 168,000 million tons, or about 580 times the annual output in 1913. (Interim Report Electric Power Supply in Great Britain, Cd. 1880, 1917.) From this available supply, an average of approximately 260,000,000 tons is raised per year, and of this quantity from 70-80 per cent. is used for home consumption for all purposes. Of this coal only about 20 per cent. is used in by-product processes.

The following table shows the allocation of the coal used in such by-product processes :—

Year.	Coal Carbonised at		Coal Gasified in Recovery Processes.	Coal Consumed in By-Product Processes.	Percentage Total Home Consumption.
	Gas Works.	Coke Ovens.			
	Tons.		Tons.	Total Tons.	All Purposes.
1911	34,460,640		713,797	35,174,437	19·03
1912	16,931,580	16,735,741	784,899	34,452,223	19·73
1913	17,753,115	19,730,829	829,045	38,312,989	20·26
Annual Average for Period 1911-13	35,203,969		775,913	35,979,882	19·68
1917	18,821,483	20,479,021	941,296	40,241,800	20·14

The remaining 80 per cent. of home consumed coal is employed for domestic and power heating purposes, these consuming respectively 20 and 60 per cent.

If we assume that coal used in by-product recovery is being used economically, i.e., without the waste of any of the combustible matter, the conservation of our coal supplies and the solution of the present fuel problem, dependent upon the supply of a cheap coal or coal substitute, and its efficient utilisation, may be said to rest upon the following three essentials :—

(1) The winning of the coal from the earth in the most economical way.

(2) The working of existing power plant upon some scientific basis to obtain the maximum energy from the coal employed, and the continual replacing of

present power plant, by proved plant of greater efficiency.

(3) The provision of a suitable smokeless fuel.

Suggestions have been put forward by eminent scientists regarding the winning of coal from the earth other than by the laborious methods of mining at present in vogue. The majority of these suggestions have proved to be impracticable with our present knowledge, the outstanding difficulty being that of surface support. If this difficulty could be overcome, and if, further, an extremely cheap solvent for coal could be discovered, from which solution the coal could be readily obtained, it is conceivable that the coal mining industry would become parallel to the salt industry of Northwich and district. The carbonisation of coal in situ has been suggested, but this is equally impracticable, and it appears that the present methods of winning the coal by direct means cannot be bettered, beyond the employment of the latest mechanical and electrical devices.

Having then obtained coal upon the earth's surface, is it possible so to alter and fit our present-day requirements and ideas to more economical methods of obtaining the maximum energy from the coal? This question has been exercising the most advanced minds of our scientific and administrative worlds for many years, and involves considerations far removed from the actual obtaining of the energy, so far removed indeed, as the psychology of the average English housewife.

Electricity, both as a prime mover and as a heating agent, together with its ease of transmission, has raised great possibilities, and the vista opens out, of our coal fields being converted into large power areas, in which the thermal energy available in coal will be transformed into electrical energy, which will be distributed to run our transport, heat our homes, and literally to do our work, and be our very life.

Such a vision is particularly attractive, and indeed, although it will take many years to move us to such accomplishments, and to allow us to overcome the difficulties attendant on the generation of such enormous centralised power and its distribution, yet it presents a practical outcome to the fuel problem. The trend of modern science is surely set in this direction, the prominence which was recently given to the Severn Scheme for the harnessing of water power being but a reflex of such a vision.

Under existing conditions, steps can, however, be taken in our present coal fields to economise, beyond the economies possible in mechanically bringing coal to the earth's surface. All coal seams are accompanied by minerals of an inferior quality, such as shales, bastard cannels, and mineral matter containing a certain percentage of carbonaceous material which are now regarded as waste. Little has been done to endeavour to recover from such minerals their valuable products, and an enormous quantity of these low grade materials is yearly dumped around the pit-heads of our collieries, disfiguring the country and wasting the power employed in their excavation. Investigations by individual workers upon such material have been made, two of which are worthy of mention, viz., T. F. Winmill, The Low Temperature Distillation of Inferior Coals, J.Soc.Chem.Ind., 1917, 36, 912, and Hoo Cannel, F. S. Sinnatt and M. Barash, Lancs. and Cheshire Coal Res. Assoc., Bulletin No. 6, and it is to the extension of such work that we must look for the contribution which those directly interested in the coal fields may make to the solution of our problem.

The economical working of existing power plant, and the production of a suitable domestic fuel are correlated. Despite the many appliances now available for the scientific control of combustion, and the legislation which makes the emission of heavy smoke a penalisable act, the bulk of power producers in this country are content to throw ten, twenty, and even thirty per cent. of the available heat of their fuel into the atmosphere.

It is beyond the scope of this work to deal with such controlling appliances, for a description of which the reader is referred to such works as "Coal and its Scientific Uses," by Professor Bone (Longmans), and the various publications by D. Brownlie on the subject of scientific control of boiler plants.* The provision of a suitable fuel, a fuel in short which is wasteproof in the hands of a non-scientific community is, however, a partial solution to the problem of overcoming the waste occasioned by power and heat producers and domestic consumers of coal.

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*Boiler Plant Testing. D Brownlie. Chapman & Hall, 1922.

This waste may be classed under two distinct headings:

(1) Waste of combustible matter, represented by smoke, from which valuable products can be recovered.
(2) Waste due to the destructive power of smoke.

(1) "It has been estimated that 80,000,000 tons of coal are consumed per annum in the United Kingdom at the present time for the production of motive power, and that an annual saving of 55,000,000 tons of the above quantity could be effected in the near future, if electric power supply were dealt with on comprehensive lines and advantage taken of the most modern engineering developments. A certain proportion of the coal now consumed in the production of motive power is subjected to preliminary treatment, such as carbonisation or gasification, whereby ammonia, tar, and other products can be recovered, the resulting coke or gas being used in the power plant. There is no question, however, that by far the largest part of the 80,000,000 tons is consumed in the raw state with the total loss of the potential by-products."*

Some idea of the value of these potential by-products may be obtained by a consideration of the domestic fuel consumption, and by a contrast between the present methods of carbonisation, and methods which could produce a fuel suitable alike for industrial and domestic supply, whilst recovering such products. In such consideration note must be taken of the fact that coke as at present produced in gas works practice does not fulfil the requirements of such a fuel. Briefly, such a fuel must ignite as readily as coal, evolve little or no smoke, possess a high radiant efficiency, and be as cheap as coal, as judged upon its steam-raising capacities. Further, it must not be fragile and must be easy to transport.

The quantity of coal consumed in the United Kingdom in 1913 for domestic purposes was approximately 35 million tons.† The consumption of this coal under the existing conditions, as compared with a carbonisation process which would produce a saleable, smokeless fuel, represents a loss per ton of coal used of 14 lbs. of ammonium sulphate, 18 gallons of tar, and 2¼ gallons of light spirit. On the other hand, to produce a similar quantity of smokeless fuel by such a carbonisation process would entail the carbonisation of 54 million tons of coal.

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* Nitrogen Products Committee. Final Report, p. 169.

† The last pre-war figure.

By such a system it would consequently be possible to conserve the following products:—

By-Products and Yields per Ton of Coal.	Total Yields per 54,000,000 Tons of Coal.
Ammonium Sulphate, 14 lbs. ...	337,500 tons
Tar, 18 gallons	972,000,000 gallons
Light Spirit, 2·25 gallons	121,500,000 ,,

Such a tar on distillation would yield 54,000,000 gallons of motor spirit, 54,000,000 gallons of burning and enriching oil, 1,600,000 tons of fuel oil, and 2,700,000 tons of pitch.* That is to say, a contrast may be drawn between these two situations, (1) the present situation under which coal is consumed without the recovery of any by-products, and (2) a possible situation under which all coal consumed is carbonised, providing the required quantity of a smokeless fuel, together with the recovery of enormous quantities of motor spirit, burning and enriching oil, ammonium sulphate and pitch, at the expense of the cost of such carbonisation and subsequent tar distillation, and the expenditure of an additional 20,000,000 tons of coal. Such a contrast may be represented as follows:—

Debit	Credit.
20,000,000 tons of Coal.	54,000,000 galls. of Motor Spirit.
Cost of Carbonisation.	54,000,000 galls. of Burning and Enriching Oil.
Cost of Tar Distillation.	2,700,000 tons of Pitch.
	121,500,000 galls. of Light Spirit.
	337,500 tons of Ammonium Sulphate.

The above balance sheet must embrace at the same time a full consideration of (2) the material damage effected by smoke evolved by burning coal in its raw condition. Hamilton (Scientific Treatise on Smoke Abatement, 1917) states "that the emission of black smoke from factory and other chimneys is a nuisance which seems to have been an established fact since the days of Queen Elizabeth (1558-1603), but to very recent years have we to look to find any practical and useful endeavours being made to cope with what is surely a most important national question." It was only in the year 1819, however, that this question was raised in Parliament, and subsequent committees of enquiry were responsible for the establishment of the Acts of 1845 and 1847, making the emission of black smoke from chimneys penalisable, although in these Acts and in the Public Health Act of 1875, chimneys of private dwelling houses are distinctly exempted.

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* Nitrogen Products Committee. Final Report, 1920. H.M. Stationery Office.

In view of this legislation, and the endeavours of specific bodies for the restriction and ultimate abolition of the nuisance, it is remarkable that so little progress has been made in the suppression of this evil. This is largely due to the fact that the smoke nuisance is a silent one, and that to the average person the evil is not known to any degree, whilst at the same time, large industrial interests are concerned in the production of large quantities of black smoke, and are often of a very conservative nature.

The damage consequent upon a continual pollution of the atmosphere by smoke can be considered under three distinct headings, namely, (1) damage to vegetation, (2) damage to structures, and (3) damage to the health of individuals breathing the polluted air.

Smoke consists essentially of a suspension of very finely divided soot in the air. Cohen and Ruston (Smoke, A Study of Town Air, 1912) state "perhaps the most important feature of the smoke problem lies in the nature of soot."

Soot consists chiefly of carbon, tarry matter, and ash, together with small quantities of sulphur, arsenic and nitrogen compounds, these latter often being of an acid nature. The tarry matter in the soot causes it to adhere so tenaciously to any surface with which it may come in contact, that even heavy rainfall will not detach it. The quantities of these various constituents present, varies with the nature of the coal burnt, and the place of deposition.

The following analyses (Cohen and Ruston) show very definitely the variable nature of soot from the same coal obtained from different positions in the same chimney :—

Analysis of Soot from the University, Leeds.

Constituents.	Original Coal.	Ordinary Grate Flue.	Boiler Chimney.			Top of Chimney
			Bottom	13 ft. from Base.	70 ft. from Base.	110 ft.
Carbon ...	69·30	40·50	19·24	16·66	21·80	27·00
Hydrogen .	4·89	4·37	2·71	0·86	1·44	1·68
Tar ...	1·64	25·91	0·09	0·28	0·80	1·14
Ash ...	8·48	18·16	73·37	75·04	66·04	61·80

Analysis of Domestic Soot from Winston Gardens, Headingly.

Constituents.	Original Coal.	Kitchen Flue.	Dining Room.	
			0-5 ft. from Bottom of Grate.	30-35 ft. from Bottom of Grate.
Carbon ...	76·80	52·34	36·45	37·22
Hydrogen ...	4·90	3·68	3·51	3·51
Tar	0·88	12·46	34·87	40·38
Ash	1·80	17·80	5·09	4·94

It should be noted here that the tarry matter as given in the above analyses was estimated by extracting the dried material with ether and subsequently distilling off the ether. In the case of the original coal, such extraction may appear rather misleading as tar does not exist in the free state in coal, but the figure here given represents a portion of the coal, probably a portion of the resinic constituent which is soluble in ether. On the other hand, the ether soluble portion of the soot probably represents more nearly its actual tarry constituent. The above-mentioned authorities state "that the proportion of tar is larger in the residential than in the industrial quarters of the city, varying from about 4·5 per cent. at Hunslet, the centre of a large industrial area, to over 15 per cent. at Roundhay on the outskirts of the city,"—a fact very evident from the analyses quoted above. Beyond these constituents soot contains varying proportions of acid sulphur compounds derived from the relatively small quantities of sulphur in the coal. Rideal gives an acid content calculated as sulphur trioxide in samples of soot from London, Manchester, and Glasgow, of 4·6, 4·3, and 7·9 per cent. respectively, whilst the soot falling on the glass roof in Kew Gardens contained nearly 5 per cent. calculated as sulphur trioxide. The acidity of the soot samples previously quoted as "Analyses of Soot from the University. Leeds," is as follows :—

Original Coal.	Domestic Soot.	Boiler Soot.			
		Base.	13 ft. up.	70 ft. up.	Top.
0·0	0·39	1·62	1·04	0·58	0·47

Other deleterious compounds have been discovered in soot, one of which is particularly worthy of mention, namely, arsenic. Many coals contain small quantities of arsenic, which is probably present in the coal in the form of arsenical pyrites, and arsenic has been found in samples of soot obtained from various sources. Dr Russell (The Monthly Weather Report of the Meteorological Office, Parts 1, 2, and 3, April, 1884, and August, 1885) discovered arsenic to the extent of ·0003 parts per million in London rain water, whilst Professor Delépine (Report of Royal Commission on Arsenical Poisoning, 1901, Part 1, and 1902-3, Part 2) found the following quantities present in soot from various sources :—

Source of Soot.	Percentage As_2O_3
1. South Yorks Coals	0.08
2. Soot from a Coke Stove burning Coke from Manchester Gas Works	0·4
3. Another Soot from Coke	0·5

Further, town dust and town air are never wholly free from arsenic. The quantity of soot deposited in any locality is dependent on the domestic and industrial consumption of coal in any such locality. Experiments have shown that the ratio of the deposit of soot, taken at two stations in Leeds, one situated at Roundhay in the country, and the other at Hunslet, an industrial area, is almost exactly 1 to 24, which approximates to a ratio of total suspended matter in the respective localities of 1 to 17.

W. Irwin (J.Soc.Chem.Ind., 1902, 21, 533) calculated from an examination of a soot deposit in Cheetham Hill, Manchester, that over an area of 100 square miles around Manchester Town Hall, 30 tons of soot fell to the ground in one day, whilst it is stated that an average of 260 tons of soot per square mile, per annum, fell in London (H. A. Des Vœux and J. S. Owens "Lancet," Jan. 6th, 1912). The above figures, based upon reliable information, give some small idea of what the total soot-fall over the whole of England must be, particularly over such large areas as those of the industrial portion of Lancashire, and of the steel and pottery districts.

The effect of the emission of such large quantities of soot may be seen from the following considerations of its effect on vegetation, buildings and structures, and health.

The Effect of Smoke on Vegetation

The assimilation of the carbon dioxide in the air by plants and the compensating emission of oxygen, takes place by virtue of the stomatal openings in the leaves of the plants. This interchange of gases is vital to plant life, and should such openings become choked by matter, the plant suffers accordingly. Blackman and Brown (Phil. Trans., 1895. 185. 502) (Proc. Royal Soc., 1902. A. 70. 397) (Proc. Royal Soc., 1905. B. 76. 402) have shown that a thin coating of vaseline over a leaf surface completely prevents such interchange of gases, and a coating of the tarry deposit from soot acts in a similar way. The further retardative action of smoke upon vegetation is dependent upon the influence of smoke upon the intensity of light, and upon the sulphuric acid content of the soot.

On the other hand, the increased carbon dioxide content of the air in industrial areas acts as a stimulant to plant growth, but such increase is so slight as to be altogether negatived by the retardative factors before mentioned. Cohen and Ruston (*ibid.* p. 33) give definite measurements of the gradation in sunlight from the outskirts of Leeds to the centre of the city directly dependent on the smoke content of the atmosphere, and photographs are reproduced showing the destructive effects of sulphur acids upon plant growth, and the cumulative effect of the products of combustion of raw coal present in varying proportions in the several localities.

The Effect of Smoke on Structures

As previously mentioned, soot clings to structures by virtue of its tarry constituent. The sulphuric acid in the soot, and also such acid as is in the free state in the air, rapidly attacks mortar, masonry, and metal work, and this corrosive action is often evident by the formation of a white deposit. Such deposit is mainly produced by the calcium and magnesium compounds in the stone or mortar combining with sulphuric acid present in the atmosphere. This destructive action is, of course, dependent on the nature of the stonework attacked, and in some cases penetration by the sulphuric acid is very deep. Prof. Jackson, King's College, London, states that on examination of the stonework from one building "The amount of calcium sulphate taken $\frac{1}{8}$ inch from the surface varied from 3·2 to 33·5 per cent.," whilst "in one case calcium sulphate was found at a depth of nearly $\frac{1}{2}$ inch, but there was no change below that." Further, the penetration by sulphuric acid considerably lessens the resistance of the stonework to atmospheric conditions, the stonework becoming much more readily attacked by carbon dioxide and water, as well as by frost, rain, and wind.

Aluminium silicate and calcium carbonate, as binders for the siliceous matter (quartz, etc.) present in stone, are rapidly attacked by sulphuric acid, and their conversion to the sulphates, which are soluble in water, renders the siliceous matter readily displaceable by the natural mechanical agencies previously mentioned. The destructive action of sulphuric acid is supplemented by the disfiguration of stonework by the tarry matters contained in the soot, and the contrast between buildings in a smokeless climate, and those in any of our large cities is so evident as to make further remark on this point unnecessary.

The above effects are equally applicable where metal work is considered, and Cohen and Ruston (*ibid.* p. 45) to show the effect of a smoky atmosphere on iron rails quote an interesting table which was compiled by W. B. Worthington, chief engineer of the Midland Railway, and A. Rattray, chief engineer of the Lancashire and Yorkshire Railway. The rails were of the ordinary railway section, weighing 86 lbs. per yard, and were placed in suitable positions alongside the line. Observations were made of the loss in weight at intervals covering considerable periods.

	Loss of Weight in Pounds per annum per yard.	Number of Years over which Observation extended.
1. In the centre of the town	1·04	17
2. In a dry place in a smoky tunnel	1·48	13
3. In a wet place in the same tunnel	1·71	8
4. On the sea coast amongst sandhills	0·18	17

The Effect of Smoke upon Health

Any direct measurement of the effect of an atmosphere polluted by smoke upon health, is a difficult one to obtain on account of the numerous factors which play an important part in the health of any community. Climatic, geographical, and particularly economic conditions are so varied in many districts, whilst, at the same time, the standards of sanitation, directly bearing upon diseases, particularly infectious diseases, are so largely dependent upon the educational status of the community, that any such measurements must be based largely upon the effect of the constituents of smoke upon animal life, and a tracing of such effects in the mortality statistics of districts, which approximate, as nearly as possible, with the conditions enumerated above.

Dr. Ascher (Smoke, a Study of Town Air—Appendix A) gives an illuminating table contrasting two towns of the same size at no great distance from one another, in the industrial district of Westphalia, which are built in the same style, differing only in the amount of coal smoke in the air, namely, Hamm and Gelsenkirchen. Hamm, being situated on the east fringe, receives only coal smoke from the west; Gelsenkirchen, being in the centre, has an atmosphere constantly charged with smoke. The table is as follows:—

1900-1902.	Death-rate per 10,000.	
Classified according to Age	Hamm (East Border) 32,435 pop. 30·6 N.T.*	Gelsenkirchen (Centre) 37,834 pop. 57·4 N.T.*
0– 1 year	228·9	258·9
1– 5 years	57·1	131·1
5–10 years	6·5	17·3
10–15 years	1·8	2·6
15–60 years	10·7	34·7
60 and over	140·4	210·2

* N.T.—Death-rate from lung diseases which are non-tubercular.

The increase in the death-rate from non-tubercular diseases, at all stages of life, due to smoke pollution, is here very evident. Prof. Delépine (Report of the Royal Commission on Arsenical Poisoning, Part 1, p. 195) states, "I have a suspicion that soot from towns, where arsenical coal is used, is far more irritating to the lungs than pure coal dust. The reason why I say so is that I have noticed there is generally more fibrous tissue produced in the lung in town anthracosis than when the coal is inhaled as dust, as, for instance, in the case of coal miners. I find the lungs of coal miners may become as black as soot and all the lymphatic vessels entirely distended with ordinary coal dust without there being any evidence of very distinct inflammatory reaction; whilst on the contrary, in towns, where the amount of carbon collected in the lump is smaller, there are frequently capsules of fibrous tissue in the lungs around small masses of carbon which have accumulated, indicating some irritating action on the part of the soot." Dr. C. W. Saleeby, at the British Commercial Gas Association Conference, October 28th, 1919, gave a remarkable condemnation of the burning of raw coal, particularly demonstrating the effects of a smoky atmosphere upon infant mortality, and laying down, very definitely, that it was the root cause of acute lung disease.

How far smoke is either directly or indirectly responsible for many of the other diseases which are common, it is impossible to say, but the evidence already quoted serves only to show, in some small measure, the ravages which are occasioned in the health of a community by breathing a smoke-laden atmosphere.

CHAPTER II

THE CONSTITUTION OF COAL

NATURE OF COAL—CLASSIFICATION OF COAL—COMPOUNDS PRESENT IN COAL—VITRAIN, CLARAIN, DURAIN, FUSAIN—COKING AND NON-COKING COALS—DISTILLATION AND DESTRUCTIVE DISTILLATION—EFFECT OF DESTRUCTIVE DISTILLATION OF COAL, AND ITS BY-PRODUCTS—NITROGEN IN COAL—DISTRIBUTION OF NITROGEN IN BY-PRODUCTS—SULPHUR IN COAL—DISTRIBUTION OF SULPHUR IN BY-PRODUCTS.

Nature of Coal

In order to understand thoroughly the fundamentals of low temperature carbonisation processes, it will be necessary to discuss the nature of coal and the effect of heat upon it. Since coals vary considerably, it is only to be expected that they would behave differently upon carbonisation, and it is this fact alone which is responsible for many of the difficulties encountered in the carbonisation of coal.

No satisfactory and comprehensive definition of coal has yet been formulated, but one fact has been established that all true coals have, as their basic foundation, bodies which have been formed from plant life. This fact was recognised long before any systematic investigation of the coal substance was made, Stopes and Wheeler stating that " so early as 1598 Matthiolus, in correspondence with Klein, remarked on the origin of brown coal from wood," whilst many other early workers acted upon the same assumption.

Recent work has, however, been able to show actual plant remains in coal, Witham (1833) being the first pioneer in the microscopical examination of coal, whilst in the preparations of Lomax, Stopes, White, and Thiessen, the several elements of plant life which have withstood the transmutation process from plant life to coal are easily discernible.

From such microscopical work, much has been discovered about the actual nature of coal, and a special branch of fossil botany has grown. Those desirous of obtaining further knowledge upon this subject are referred to "Studies in Fossil Botany," by D. H. Scott.

The definition of coal adopted by Stopes and Wheeler, ("Constitution of Coal," H.M. Stationery Office, 1918), accompanied by the subsequent qualifications which they make with regard to veins, partings, and extraneous inorganic matter, and with regard to cannels and kindred minerals, is perhaps the most satisfactory so far laid down. They define coal as "a compact, stratified mass of mummified plants, (which have in part suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter." Furthermore, "according to this definition, unless the accretion of the plant substance is so pure and free from other matter (mineral detritus, etc.) as to be *substantially a deposit of plants alone*, it is not a coal. Cannels form a partial exception to this rule: in these both the micro-animals of plankton and occasional fish were involved at times in the accumulation."

Classification of Coal

Coals vary considerably according to the manner of formation, their geological age, and the many factors, such as temperature and pressure, which have operated during such formation. Consequently, many attempts have been made to grade all types of coal upon some common basis according to (1) their varying properties, (2) the proportion of the several common elements which they contain, (3) the geological age of their formation, or (4) their commercial application. All types of coal show a gradual merging into one another, and there are no definite limits for any class of coal. All coals consist essentially of a base of carbon, hydrogen, and oxygen, together with smaller quantities of nitrogenous and sulphur compounds, and the constituents of the coal ash (i.e., silica, iron, aluminium, magnesium, manganese, calcium, alkalies, etc.). Coals appear to show a definite gradation from plant life through peat to lignite or brown coal, bituminous coals, anthracite, and as a final degradation product, pure graphitic deposits. Such a gradation, attractive though it may seem, has not been fully realised by scientific investigations, although the sequence is maintained as a basis of classification.

Regnault (1837) based his classification upon the oxygen content of coals, naming five distinct classes of coal, viz.: (1) Anthracites, (2) Fat hard coal, (3) Fat soft coals, (4) Fat coals with a long flame, (5) Dry coals with a long flame, this classification finding particular application in the industrial use of coal.

Field advanced a classification on the proximate analyses of coals, whilst upon the terminology here advanced and modified by later investigators, the United States' Geological Society adopted the following classification, based on the ratio of carbon and hydrogen present in the coal :—

Class.	Ratio C/H.
Anthracites	30-26
Semi-anthracites	26-23
Semi-bituminous	23-20
Bituminous I.	20-17
Bituminous II.	17-14·4
Bituminous III.	14·4-12·5
Bituminous IV.	12·5-11·2
Lignites	11·2-9·3

A more complete classification, employing the same means of differentiation, viz., the percentage of carbon and hydrogen in the coal, was advanced by Seyler, who studied in particular South Wales coals. Seyler's classification, as given by Illingworth (The Analysis of Coal and its By-Products) is shown in the following table :—

SEYLER'S CLASSIFICATION OF COALS.

	Anthracite.	Carbonaceous.	Bituminous Carbon Plane.			Lignitious.
			Meta-	Ortho-	Para- East Coals.	
	C. over 93·3	93·3-91·2	92·2-89·0	89·0-87·0	87·0-84·0	84·0-80·75
Per-Bituminous Genus. H. over about 5·3 Volatile over 30%			Per-Meta-Bituminous Species. North Country Steam Coals. Over 5·7 30-44	Per-Ortho-Bituminous Species. Bastard Cannels. Gas Coals. Over 5·7 Over 36	Per-Para-Bituminous Species. Cannels. Over 5·8 Over 40	Hard Steam Coals.
Bituminous Genus. H. about 5·0 5·8 Volatile 23-40		Pseudo-Bituminous Species. 5·0-5·8 Over 23	Meta-Bituminous Species. Welsh Coking Coals. 4·9-5·7 23-30	Ortho-Bituminous Species. Durham Type of Coking Coals. Smithy and Gas Coals. 5·0-5·7 28-36	Para-Bituminous Species. Coking Coals and Best Gas Coals. 5·0-5·8 steams 30-40	
Semi-Bituminous Genus. H. about 4·5-5·0 Volatile 16-24		Ortho-Semi-Bituminous 2nd Admiralty Species. Steam Coals (Coking) Higher Index Blended for Coke. 4·45-5·0 14-24	Sub-Meta-Bituminous Species. Index 8-17. House Coal Continental Coking Coal when Index high. 4·5-4·9 16-23	Sub-Ortho-Bituminous Species. Coking and Steam. 4·5-5·0 16-23	Sub-Para-Bituminous Species. ?-5·0 16-29?	
Carbonaceous Genus. H. about 4·0-4·5 Volatile about 10-16	Semi-Anthracite Species. Dry (non-caking) Steam 4·0-4·5 9-15	Ortho-Carbonaceous Admiralty Species. Welsh Smokeless Steam. Slight Caking. 4·20-4·45 10-14	Pseudo-Carbonaceous Species. Sub-Meta-Bituminous Steam Coals. 3·7-4·5 10-16	Sub-Ortho-Bituminous pseudo Carbonaceous Species. ?-4·5	? ?	
Anthracite Genus. H. under about 4·0% Volatile under about 10%	Ortho-Anthracite Species. True Anthracites. Under 4·0 5·9	Sub-Carbonaceous pseudo-Anthracite. Dry Steam (non-caking) bastard Anthracites. Under 4·2 Under 7·7	Sub-Meta-Bituminous pseudo-Anthracite Species. Under 3·7 Under 10	? ?	Sub-Para-Bituminous pseudo-Anthracite Species. Under 4·2 Under 10	

Classifications based upon the chemical elements of a coal are inadequate, serving only to divide the general broad classes of coal, whereas a true classification should embrace the physical properties, and their behaviour according to their industrial application.

Lewes' suggested scheme of classification of coals according to the compounds actually present in the coal substance, appears to provide the line along which the true classification will eventually be evolved. In coals, certainly two, and probably more types of compounds are present.

The two classes of compounds already diagnosed have been termed the resinic and cellulosic, the resinic being those compounds representative of the gum and resin bodies in the plant, and the cellulosic of the degradation products of the cellulose portion of the plant.

Lewes assumes the presence of four types of compounds, as follows:—

Compound.	Percentage Composition. C	 H	 O
A. Carbon residuum	100	—	—
B. Humus compounds	62	5	33
C. Resin compounds	79	11	10
D. Hydrocarbons	96	4	—

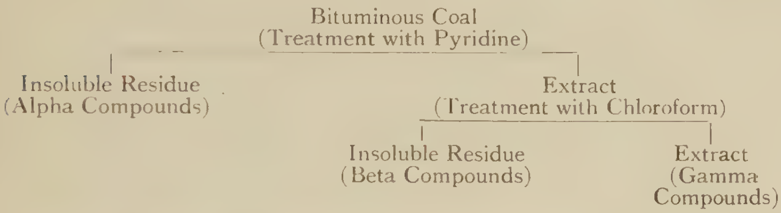
Upon such assumptions, coals may be classified as follows upon the basis of Gruner's classification :—

	Carbon Residuum.	Humus Bodies.	Resin Bodies.	Hydrocarbons.
I. Flaming A+2B+C+D	20·0	40·0	20·0	20·0
II. Fat gas A+B+2C+D	25·0	25·0	25·0	25·0
III. Furnace 2A+B+2C+2D	28·6	14·2	28·6	28·6
IV. Coking 3A+B+3C+3D	30·0	10·0	30·0	30·0
V. Steam 3A+2C+D	50·0	—	33·4	16·6
VI. Anthracite 5A+2C	71·4	—	28·6	—

The above cannot be regarded as representative of the actual facts, for research work has not yet definitely established the nature of the bodies as they occur in the coal, but as representing a line or direction of classification the above is distinctly interesting.

Compounds Present in Coal

Coal is an extremely difficult substance to attack in such a way as to yield information as will lead to a knowledge of the constitution and nature of the coal substance. Ordinary chemical reagents either fail to attack the coal substance, or yield such complex products that deductions from a consideration of the nature of such products is almost impossible. Recently, however, a promising avenue has been pursued in the study of the action of solvents upon coals. Even here, some doubt is expressed as to whether the action is wholly a solvent one or whether some slight chemical reaction takes place between the solvent and the coal. By the use of pyridine and chloroform, the following separation has been effected, using a bituminous coal:—



Jones and Wheeler have termed the alpha and beta compounds cellulosic, being of a similar type, whilst the gamma compounds have been termed resinic. Chemical examination of these several products have been made, resulting in the elucidation of some of the groupings and radicles which are present in these compounds, but it is beyond the scope of this work to enter into a discussion of them. Recently Bone (Proc.Roy.Soc., 1922, A. 100, 582) has published the results of work upon the action of solvents on coal, for details of which reference should be made to the original paper.

Vitrain, Clarain, Durain, and Fusain

Another line of attack which promises an extension of our knowledge of the coal substance proper, is the separation made originally by Stopes (Proc.Roy.Soc., 1919, B. 90, 470). Stopes distinguishes four distinct constituents in coal, which she has termed respectively, vitrain, clarain, durain, and fusain. These types are distinguishable by visual supplemented by microscopical examination.

The following is a brief description of each of these several constituents:

(*1*) *Vitrain*

Stopes states that vitrain occurs in narrow bands, rarely exceeding 8 millimetres in thickness, whereas Sinnatt (Journ. Soc. Dyers and Col., 1921, 37, 108) states " that in samples of Lancashire coals bands ½ in. in thickness are common, and that in one of the samples exhibited, the whole mass of the lump, 3 or 4 ins. in thickness, appeared to correspond to the description of vitrain by Stopes." Vitrain is characterised by its extreme lustre, by the fact that it appears to possess a structure breaking upon pressure into small cubical pieces, and by the absence of plant remains when examined microscopically.

(*2*) *Clarain*

This is somewhat difficult to differentiate from vitrain. Stopes states that " it has a definite and smooth surface when broken at right angles to the bedding plane, and these surfaces have a pronounced gloss or shine." Clarain is slightly less lustrous than vitrain, but whereas vitrain appears fairly homogeneous when examined microscopically, clarain shows the presence of disintegrated plant remains, such as leaf tissue, microspores and megaspores, together with resin-like bodies.

(*3*) *Durain*

In contrast to vitrain and clarain, durain possesses a matt surface and is hard, appearing homogeneous in nature. It has a close texture and a definite grain. It is particularly characterised by the presence in it of large quantities of megaspores, with smaller quantities of microspores, which are very evident on microscopical examination.

(*4*) *Fusain*

Fusain, previously often termed " mother of coal," is the constituent which has, perhaps, attracted the attention of most observers. It occurs in bands running parallel to the bedding plane, which form lines of weakness in the coal. When exposed to the air, fusain is easily powdered, producing a black powder which possesses a silky touch. On microscopical examination, it is seen to be composed of minute log-like particles, with very clearly cut surfaces, which on breaking give particles which are replicas of the parent particle. This portion of coal is generally recognised as the portion which soils the hands. Fusain is extremely difficult to wet out with water, fusain which has been ignited not being quenched when thrown on the surface of water.

These several constituents have been more completely examined, and for the results of these further examinations the reader is referred to the bibliography (page 227).

Coking and Non-Coking Coals

The property which certain coals exhibit of forming coherent coke on carbonisation, and the type of coke produced, is dependent on the nature of the coal and on the method of carbonisation.

Certain bituminous coals, anthracite, and coals of an anthracitic nature do not give a hard, coherent coke, under normal conditions of carbonisation. Speaking generally, coals rich in carbon and having a low oxygen content, or coals possessing an abnormally high oxygen content (exceeding 15 per cent.), or which have already undergone oxidation, are non-coking coals.

Coals may be classed according to their coking properties as gas-coals, coking coals, steam coals and anthracites.

Under this classification, the volatile organic matter at 900° C. calculated on a moisture and ash-free basis, indicates approximately the type of coal; gas coals yielding from 32-38 per cent., coking coals from 20-32 per cent., steam coals, which are non-coking, from 10-20 per cent., whilst coals below 8 per cent. can be regarded as anthracitic in nature.

For the production of coherent coke at a low temperature, a particular type of coking coal must be used, or the coal must undergo a pre-treatment, such as blending or heating, prior to carbonisation, within a limited range of temperature (see page 80).

Non-coking coals can be utilised in low temperature carbonisation processes producing a pulverulent fuel for use, either as such in powdered fuel or producer plant, or by subsequent briquetting, the coke can be made suitable for domestic and general steam raising purposes.

Coals which give coherent coke on carbonisation have been resolved into compounds according to the solvent action of pyridine and chloroform upon them. Illingworth (The Analysis of Coal and its By-Products, p. 112) states that the portion soluble in pyridine and chloroform—namely the resinic constituent—is responsible for the coking property of coal, and must be present to the extent of 5-6 per cent. by weight of the coal, for such coal to produce a coke.

Bone and his collaborators (Proc.Roy.Soc. 1922, A. 100, 582: Wheeler, Fuel, April, 1922, 61) are opposed to this view, concluding that the " free resin disseminated through the coal substances,"—the portion soluble in pyridine and chloroform, is not responsible for the coking properties of a coal.

The further relationship between coking property and the alpha, beta and gamma compounds of a coal is dealt with in a description of the Illingworth Process (page 142).

The banded constituents of a coal have varying caking propensities, durain and fusain being non-coking, whilst vitrain and clarain possess coking powers, dependent on the nature of the coal of which they form a part.

Various laboratory methods have been suggested with a view to determining the caking power of a coal under standard conditions, for an account of which the reader is referred to a paper by F. S. Sinnatt and A. Grounds, on " The Determination of the Agglutinating Power of Coals " (J.Soc.Chem.Ind. 1920. 39. 83T.), and to a method for " The Determination of Caking Index," by S. Roy Illingworth (The Analysis of Coal and its By-Products, p. 117).

Distillation and Destructive Distillation

Having described the raw material, a brief account of the products formed when coal is heated out of contact with air will indicate the nature and complexity of the process of destructive distillation of coal.

A distinction must be clearly recognised between distillation and destructive distillation. In distillation *per se* the resultant products, obtained by heating a substance and condensing the volatile portions driven off, are present as such in the original substance, e.g., distillation of ether, water or alcohol. In destructive distillation, the resultant products are different both chemically and physically from the products present in the original substance, e.g., coal, wood.

Coal cannot be distilled to obtain coal as a distillation product,. since, on distillation, it breaks up into complex products which do not resemble coal chemically and physically.

From the resultant products of the destructive distillation of coal, the fullest knowledge of the coal substance and its greatest and most economical utilisation has resulted.

The Effect of Heat on Coal

The effects of heat on coal are very varied, the products differing greatly according to the nature of the coal and the temperature to which it is heated. Coal is a very active substance, freshly mined coal, and exposed coal in situ, continually giving off gases, and absorbing or reacting with oxygen from the air. Many investigators have studied both the emission of gas from coal at normal temperatures and the affinity which exists between coal and oxygen. The following analyses (Horace and Porter, U.S. Geological Survey, 1907-08) show the nature of the gas given off from a sample of coal over a period:—

Coal No. 23.

Time in Storage.	CO_2	O_2	CO	CH_4	H_2	N_2
	Immersed under water.					
4 days . . .	0·3	2·5	0	1·3	—	95·9
6 days . . .	0·0	0·5	0	6·8	—	92·7
10 days . . .	0·3	0·2	0	15·9	—	83·6
13 days . . .	0·3	0·3	0	32·0	—	67·4
16 days . . .	0·4	0·3	0	74·9	—	24·4
104 days . .	0·8	0·0	0	95·7	—	3·5
Coal No. 23	Dry in closed bottles.					
10 days . . .	0·5	0·0	0	18·9	—	80·6
34 days . . .	0·0	0·1	0	73·3	—	26·6
71 days . . .	0·6	0·3	0	72·0	—	27·1

The affinity, which coal exhibits for oxygen, results in distinct changes in coal which is stored for a considerable period with access to air, and depends upon the proportion of certain easily oxidised constituents in the coal. Such affinity is directly responsible for a small loss in the heating value of a coal, for a reduction in its coking properties, and, under certain conditions, for the spontaneous combustion of coal.

Mahler (1913) states that when coal is heated to 200° C. in contact with air, small quantities of formic and acetic acids, acetone and methyl alcohol are produced, whilst Burgess and Wheeler (1914) stated that whereas the water formed by heating coal at 100° C. was pure, that obtained by heating the coal at 250° C. showed the presence of acetic acid only, whilst at 300° C. a small quantity of an acid liquor containing hydrocarbons was produced. Experiments which have recently come to the authors' notice have shown definitely that coals undergo a special type of oxidation at temperatures as low as 170° C., producing ketones, alcohols and aldehydes.

Burgess and Wheeler (1914), summing up the action of heat upon a bituminous coal, give the following sequence of events prior to the temperature of about 350° C., which is regarded as the decomposition temperature of coal, i.e., the temperature at which the coal definitely begins to split up into new compounds. Occluded gases were evolved in small quantities up to 150-200° C. These gases consisted mainly of the higher members of the paraffin series of hydrocarbons (ethane, propane, butane, etc.). At 200° C., a copious evolution of water occurred which continued up to 450° C., marking a definite decomposition point, whilst the gases evolved during the maximum water evolution contained a high percentage of the oxides of carbon. At 270-300° C., an organic sulphur compound decomposed and from 270-350° C. the gases evolved contained a considerable proportion of olefines (ethylene, etc.). At 310° C., a thin, reddish brown oil appeared, whilst at 350° C., a rapid and copious evolution of gas together with much viscid oil occurred.

Prior to the above decomposition point (about 350° C.), it must be clearly recognised that coal undergoes a certain amount of decomposition by oxidation as is mentioned previously, and, furthermore, heat alone modifies the properties of a coal below this decomposition point.

Delesse gives the following decomposition points:

(1) Peat about 250° C.
(2) Lignite about 300° C.
(3) Coal about 400° C.

and these temperatures have been shown by later investigations to be approximately correct.

The following table given by Anderson is illustrative, as indicating the effect of heat at temperatures lower than 350° C. He heated coals in a current of dry CO_2 at about 300° C.

	Ell.	Splint.	Gas.	Bannockburn Main.	Kilsyth Coking.
Relative coking power before heating . .	4	3·5	3·5	15·5	16
Loss in weight on heating: percentage on dry coal .	9·5	16·2	21·8	7·3	6·4
Result of coking test on heated coal .	Chiefly a dull earthy coke. The rest powder.	The residue after coking just cohered and no more.		Good coke but of dull appearance.	

Work upon the decomposition of coal above this accepted decomposition point has been carried out by recent workers *in extenso*, and two pioneering series of research, namely that by Burgess and Wheeler (Trans. Chem. Soc., 1910, 97, 1907; 1911, 99, 649; and 1914, 105, 131) and that by H. C. Porter and G. B. Taylor (The Primary Volatile Products of the Carbonisation of Coal, U.S. Bureau of Mines, Bull. 141), together with work carried out by other investigators both in the laboratory, and on large plant, show perfect agreement in the results, but much difference of opinion in the interpretation.

On being heated above its decomposition point, coal gives rise to two distinct portions: (1) a non-volatile portion consisting of coke and (2) a volatile portion consisting of water, tarry matter and gas. The nature and the chemical composition of these two portions show considerable variation according to the temperature to which the coal is heated, the several elements in the coal (carbon, hydrogen, oxygen, nitrogen and sulphur) grouping themselves into different compounds. The nitrogen and sulphur are dealt with later (pp. 28-39). The non-volatile portion of the coal contains more carbon than the original coal, whilst the volatile portion contains a higher percentage of hydrogen than the original coal.

The following is a résumé of the results of scientific investigations upon the nature of these several products. Porter and Taylor (*loc. cit.*) state that:—

(1) Oxygen-bearing substances of a cellulosic nature first break down yielding water, carbon monoxide and carbon dioxide.

(2) Decomposition, yielding paraffin hydrocarbons, both liquid and gaseous, begins at an early stage.

(3) The lower the percentage of oxygen in the coal, the higher the proportions of hydrocarbons and tar in the volatile matter.

(4) In the case of a sub-bituminous coal the "water—CO_2" reaction predominates up to temperatures of 450° C.

Burgess and Wheeler (*loc. cit.*) summarise their work as follows:—

(1) Evolution of hydrocarbons of the paraffin series ceases almost entirely at temperatures above 700° C.

(2) Ethane, propane and butane, and probably higher members of the paraffin series form a large percentage of gases evolved below 450° C.

(3) For all coals, whether bituminous, semi-bituminous or anthracitic, there is a well-defined critical temperature between 700 and 800° C., corresponding to a rapid increase in the hydrogen evolved.

(4) With bituminous coals, such increase falls off at a

temperature above 900° C., with anthracite coal it is maintained to 1100° C.

The temperature which Burgess and Wheeler give as the temperature at which the hydrocarbons of the paraffin series almost cease to be evolved, i.e., about 700° C., may be regarded as the temperature which marks a definite transition point in the decomposition of coal, the products from the temperature below and about this point possessing characteristic properties and chemical compositions distinct from those of the products obtained at temperatures above this point.

This temperature may be regarded as the distinctive temperature between what is termed low-temperature distillation or carbonisation on the one hand, and low-high and high temperature distillation or carbonisation on the other.

The products of high and low-high temperature carbonisation are formed through the interaction and reaction of the products driven off from the coal at low temperatures, and from a further decomposition of the non-volatile portion of the coal when such portion is submitted to higher temperatures. Lewes (Cantor Lecture, Roy.Soc.Arts, December 18th, 1911) sums up these secondary reactions in the following words:

"At about 400-450° C. the secondary reactions start, the saturated hydrocarbons split up into unsaturated and simpler members of the saturated series, the hexahydrides shed hydrogen and give aromatic hydrocarbons, the tar thickens and alters in character, and synthetic reactions start, cresol and hydrogen form more toluene, and carbolic acid and carbon yield carbon monoxide and benzene. At about 900° C., the degradation of all the hydrocarbons and other oxygenated bodies is proceeding and finally the mixture of the result of endless actions and reactions yields us the high temperature gas and tar; the mixture being diluted with the carbon monoxide, hydrogen and methane yielded by the decomposition of the residues left in the soft coke, which leaves the hard coke behind."

The products of the low temperature carbonisation of coal are as follows:—

(1) A coke which contains a proportion of volatile constituents, which can be driven off at higher temperatures. Such a coke ignites easily, burns without smoke and tends to be a more friable and softer coke than that obtained from the same coal at higher temperatures.

(2) A tar which is characterised by its low specific gravity (approximating from 0·995 to 1·08), its low free carbon content and its liquid nature, yielding a fairly high proportion of light distillates of a paraffin nature, and oils containing a high percentage of tar acids.

(3) A gas containing a high percentage of methane and saturated hydrocarbons, and of a very high calorific value.

Nitrogen

Nitrogen is present to a certain extent in all coals, the actual amount varying from 0·5 per cent. to about 1·9 per cent., a normal figure for an English bituminous coal being about 1·4 per cent. to 1·7 per cent. Although at first sight, this would appear to be only a very small quantity, it is, nevertheless, very important, being the source of all the ammonium sulphate produced in gas works, by-product recovery coke ovens and by-product producer plants.

If we consider a coal which contains 1·5 per cent. of nitrogen and suppose that, by suitable treatment, the whole of the nitrogen were converted into ammonia and subsequently into ammonium sulphate, then each ton of coal would yield 40·8 lbs. of ammonia gas, corresponding to no less than 158·4 lbs. of ammonium sulphate—an item of considerable interest from the economic point of view of coal distillation, considering the value of this by-product as a fertiliser. Unfortunately, however, in actual practice, the yield of ammonium sulphate per ton of coal treated is very much below this figure, the reason for which will be given later. The following figures (Nitrogen Products Committee Final Report, pp. 99-101, H.M. Stationery Office, 1920) indicate the average yields of ammonium sulphate per ton of coal in the various industries carbonising coal:—

Industry.	Year.	Lbs. Ammonium Sulphate per Ton of Coal.
Gas works	1917	22·4
Gas works	1911-13	22·7-23·0
Coke ovens (all types)	1917	18·0
Coke ovens (recovery types)	1917	24·0
Gas producers	1917	66·3
Gas producers	1911-13	84·8

It must be pointed out that the actual amount varies with individual works, depending on the type of plant and its efficiency, whilst the kind of coal treated is also a very important factor governing the yield of ammonia produced.

Very little is known concerning the nature of the nitrogenous bodies present in the coal substance, but it would seem that the nitrogen is combined with carbon, hydrogen, oxygen and possibly sulphur, forming many complex organic substances. These may be placed in two definite classes:—

(*a*) Those readily decomposed by heat.

(*b*) Those only decomposed with great difficulty, being found, perhaps somewhat altered in constitution, but still present in high-temperature coke from the gas works and coke oven.

Maillard has thrown considerable light on the constitution of the nitrogenous bodies in coal, based upon the formation of "amino-ulmins" by the condensation of several molecules of sugar with one amino-nitrogen atom, resulting in dehydration and the probable formation of cyclic groupings. As such amino-ulmins yielded pyridine bases upon destructive distillation, Maillard suggested that similar bodies occurred in coal (since coal also yields pyridine bases when destructively distilled) and that they were produced by the condensation of "sugars," constituents of the celluloses, etc., with amino-acids present in proteins. Bodies similar to these would be responsible for the "pyridine bases" present in coal tar.

Terres, in a paper dealing with the occurrence of nitrogen in coals and cokes (J. Gasbeleucht. 1916, 59, 519) describes certain experiments which tend to support the argument put forward by Maillard. Terres heated a number of organic bodies containing nitrogen at 700-900° C. in an atmosphere of carbon dioxide and found that only amino- and substituted amino-compounds yielded ammonia. Furthermore, by extracting coal with various organic solvents, e.g., benzene, chloroform and xylene, he obtained extracts which contained nitrogen; he was not able, however, to identify the nature of the nitrogen grouping. The following table indicates the amounts of nitrogen in the extracts and residues, the original coal (Saar) having a nitrogen content of 1·15 per cent.

Solvent.	Percentage Extracted.	Percentage Nitrogen in Extract.	Percentage Nitrogen in Residue.
Benzene . . .	0·32	2·3	1·07
Chloroform . .	0·39	2·76	0·95
p-Xylene . . .	0·36	2·77	0·94
Pyridine . . .	17·24	Not determined	1·06

With regard to what might be termed the "fixed" nitrogen in the coke, practically nothing is known, though one authority (Christie, Inaug. Diss. Aachen, 1918) is of the opinion that this nitrogen is present as "nitride" in the original coal. It will suffice for the present to mention that when treated in a by-product recovery gas producer, the bulk of the nitrogen is recovered as ammonium sulphate.

When coal is subjected to destructive distillation, the nitrogen distributes itself among the products of distillation yielding a variety of nitrogenous compounds, together with a certain amount of free nitrogen. The actual amounts and nature of these nitrogen compounds vary with the temperature and other conditions obtaining during the distillation, but the following table gives an idea of their diversity :—

Distribution of Nitrogen

In the Gas	Nitrogen, Cyanogen, etc.	
In the Liquor	Ammonium Carbonate	"free"
	,, Sulphide	
	,, Hydrosulphide	
	,, Cyanide	
	,, Sulphite	"fixed"
	,, Thiosulphate	
	,, Thiocarbonate	
	,, Chloride	
	,, Sulphocyanide	
	,, Ferrocyanide	
In the Tar	Pyridine, Picolines, Lutidines, i.e. "Pyridine Bases," Acridine, Aniline, Quinoline, Isoquinoline, Carbazole, Phenylnaphthyl Carbazole, etc.	
In the Coke	Nitrogenous bodies of unknown constitution	

In the foregoing list, the compounds of ammonia are the most important, though the amount of nitrogen recovered as ammonia from the distillation of coal does not exceed 20 per cent. of the total nitrogen in the coal, by far the greater amount remaining in the coke. Short (J.Soc.Chem. Ind. 1907. 26. 581) quotes figures indicating the results of large scale operations carried out on Scottish coals (per cent. nitrogen = ·915-1·873) at the Provan Gas Works, Glasgow (McLeod. J.Soc.Chem.Ind. 1907. 26. 137), and gives the following results obtained on a Durham coking coal (per cent. nitrogen = 1·57) in Otto-Hilgenstock ovens at Blaydon-on-Tyne. It must be understood that these figures deal with high temperature carbonisation, i.e., above 1000° C.

		Gas Works.	Coke Ovens.
Percentage of original nitrogen.	remaining in coke	58·3	43·31
	in tar as bases	3·9	2·98
	recovered as ammonia compounds	17·1	15·16
	recovered as cyanogen compounds	1·2	1·43
	as nitrogen in gas	19·5	37·12
		100·0	100·00

Upon altering the temperature of distillation, however, the distribution of the nitrogen among the products undergoes a marked change in many ways. Starting at low temperatures, W. C. Anderson and J. Roberts (J.Soc.Chem.

Ind. 1898. 17. 1013) showed that the temperature at which ammonia begins to be evolved varies with the coal, from 315° C. in the case of the younger coals, to 480° C. in the case of anthracite. These results have been confirmed by other experimenters and detailed figures have been published showing the distribution of the nitrogen at various temperatures ranging from 300° C. to 1200° C. The following table due to Simmersbach (Stahl und Eisen. 1914. 34. 1153 and 1209) indicates the distribution of nitrogen in the products of carbonisation:—

Silesian Coal

Ash content . . . . . 6·63%
Nitrogen content . . . . 1·39%

Temperature of Carbonisation °C.	Percentage Nitrogen in Ammonia.	Percentage Nitrogen in Cyanogen.	Percentage Nitrogen in Tar.	Percentage Free Nitrogen in Gas.	Percentage Nitrogen in Coke.
600	7·81	0·25	2·12	18·13	71·69
700	18·13	0·66	3·65	12·13	65·43
800	21·28	0·87	3·47	10·73	63·65
850	23·68	1·11	3·72	10·37	61·12
900	24·12	1·19	4·15	12·14	58·40
1000	23·15	1·23	4·11	21·53	49·98
1100	23·09	1·31	3·70	30·51	41·39
1200	22·84	1·42	4·21	45·10	26·43

Westphalian Coal

Ash content . . . . . 5·70%
Nitrogen content . . . . . 1·391%

800	19·46	0·76	1·92	5·88	71·98
850	22·14	1·10	1·77	4·93	70·06
900	19·94	1·11	1·61	9·99	67·35
1000	19·61	1·25	1·87	21·54	55·73

The corresponding yields of ammonium sulphate are indicated in the following table:—

Silesian Coal

Temperature °C.	Total Nitrogen in Coke.	Production of Sulphate. Percentage of Dry Coal.
600	1·273	0·515
700	1·218	1·194
800	1·205	1·401
850	1·187	1·562
900	1·139	1·588
1000	0·997	1·525
1100	0·830	1·520
1200	0·529	1·504

Westphalian Coal

Temperature °C.	Total Nitrogen in Coke.	Production of Sulphate. Percentage of Dry Coal.
800	1·275	1·277
850	1·243	1·453
900	1·204	1·309
1000	1·091	1·288

Recently, experiments have been carried out by Monkhouse and Cobb (Reports of the Gas Research Fellowship, Leeds, 1921 and 1922; Fuel, Sept., 1922) and by Greenwood and Hodsman (J.Soc.Chem.Ind. 1922. 41. 273T) upon the yield of ammonia from coal and coke, and upon the various factors influencing its formation and survival during carbonisation.

It is not intended to describe here, all the research work carried out upon the nitrogen present in coal, but it will suffice to give a summary of the conclusions arrived at from the various investigations :—

(1) The evolution of ammonia begins at about 315° C. for younger coals, but not until about 480° C. in the case of anthracite.

(2) The yield of ammonia gradually increases with the rise in temperature until a maximum is reached. This lies at about 800-900° C., but is slightly different for different coals. Upon increasing the temperature still further, the yield of ammonia again decreases. It will be noticed that neither low temperature nor very high temperature carbonisation tend to a maximum yield of ammonia. There are, however, several factors which considerably affect the quantity of ammonia formed by distillation. It is a well-known fact that pure ammonia gas, passed over a hot surface of broken porcelain, begins to decompose a little below 500° C. and that decomposition is complete at about 800° C.—a temperature below that at which, in coal carbonisation, the maximum yield of ammonia is produced. In the latter case, however, the ammonia is very largely diluted with other gases, with the result that decomposition only becomes apparent at about 900° C.

(3) A high speed of gas flow in the retort retards the

decomposition of ammonia by decreasing the time of contact between the gases and the hot retort.

(4) The formation of cyanogen compounds gradually increases with the temperature, being very small below 600° C. and not attaining a maximum even at 1200° C.

(5) The amount of nitrogen remaining in the coke gradually decreases as the temperature rises. The nitrogen thus removed from the coke does not, under ordinary conditions of carbonisation, go to yield solely ammonia, a large part being found as free nitrogen in the gas. If, however, steam is passed into the mass of red hot coke, the yield of ammonia is very much increased, especially at high temperatures (*vide* Fuel Research Board Report, 1920-21, " Steaming in Vertical Gas Retorts," H.M. Stationery Office, 1921). Furthermore, if the high temperature coke is gasified in a producer with the use of steam, a large quantity of the nitrogen in the coke can be recovered as ammonia. It must be mentioned that at low temperatures, say 400-600° C. the use of steam has little or no effect upon the quantity of ammonia obtained.

(6) The presence of oxygen is detrimental to the formation of high ammonia yields since it decomposes the ammonia produced. This effect is much more marked with dry air, and consequently moisture (present as steam) acts as a deterrent in the oxidation of the ammonia.

(7) Hollingworth (Gas World, March 3rd, 1917) has shown that by carbonising coal to which he added 10 per cent. of lime, at 800° C., the yield of ammonia was increased, whilst the addition of ferric oxide acted in a contrary manner. Whilst this would point to the advantage of the removal of pyrites from coal prior to carbonisation with the object of obtaining a larger quantity of ammonia per ton of coal carbonised, the addition of lime to the charge, with the same object in view, has the disadvantage of increasing the ash content of the residual coke.

(8) The amount of recoverable ammonia varies with different coals, and is not directly proportional to the total amount of nitrogen present in the original coal, although with a higher nitrogen content in the coal, the formation of a larger quantity of ammonia is fairly certain. The following table indicates the approximate amount of ammonium sulphate obtained from 1 ton of gas coal carbonised at different temperatures:—

Temperature °C.	Lbs. of Ammonium Sulphate.
300-400	6-8
400-500	11-13
500-600	14-16
600-700	16-18
700-800	18-21
800-900	22-26
900-1000	22-24
1000-1100	18-20
1100-1200	16-18

Sulphur

All coals contain sulphur in varying quantities, and, although its actual amount may be comparatively small, it is one of the chief factors in determining the usefulness or otherwise of a coal for many purposes.

The actual quantity of sulphur present may vary from traces up to 3 or 4 per cent., whilst high sulphur coals (such as certain American bituminous coals) as mined may contain even higher than this amount. It must be clearly understood that the sulphur in coal is not present as free sulphur, except in a few rare cases, but in a combined state, the following forms being present:—

(*a*) Sulphate sulphur.
(*b*) Pyritic sulphur.
(*c*) Organic sulphur.

Space will not permit of a discussion upon the origin of the sulphur compounds in coal, or their bearing (particularly of pyritic sulphur) upon the liability of a coal to undergo spontaneous combustion, but it is essential that the effect of carbonisation upon the distribution of the sulphur among the products of distillation be described. The actual proportion of the three forms of sulphur compounds does not bear any relationship to one another: or in other words, the high sulphur content of one coal may be due almost entirely to pyritic sulphur, whilst in another case, organic sulphur may be the predominating form.

Sulphate sulphur in coal is fairly common, although in actual amount it is usually very small, being present chiefly as sulphates of calcium and of iron, the latter being produced by oxidation of the iron pyrites. Sulphates in a coal have not a very deleterious action unless, of course, they are present in large amounts.

Powell (J.Ind.Eng.Chem., 1920, 12, 1069) has thrown considerable light upon the forms of sulphur in coal, and the effect of carbonisation upon them. He carbonised a Tennessee coal at temperatures varying from 300° to 1000° C. and estimated the sulphur in the various products of distillation.

The figures are given as percentages by weight on the air dried coal.

Temperature °C.	0	300	400	500	600	1000
Pyritic sulphur . .	1·75	1·75	1·42	0·31	0·00	0·00
Sulphate sulphur .	0·71	0·55	0·44	0·01	0·01	0·00
Organic sulphur .	1·79	1·63	1·51	1·70	1·87	1·81
Sulphide sulphur .	0·00	0·13	0·44	0·93	0·82	0·84
Sulphur as hydrogen sulphide . .	0·00	0·19	0·39	1·20	1·39	1·44
Sulphur in tar . .	0·00	0·00	0·05	0·10	0·16	0·16
Sulphur as carbon bisulphide . .	0·00	0·00	0·00	0·00	0·00	0·00
Total sulphur . .	4·25	4·25	4·25	4·25	4·25	4·25

From the results obtained, Powell concluded that:—

(*a*) The iron disulphide begins to decompose below 400° C. and is completely decomposed at 600° C.

(*b*) Sulphates are reduced to sulphides below 500° C.

(*c*) The organic sulphur yields some sulphuretted hydrogen as well as sulphur compounds in the tar at fairly low temperatures.

Foerster and Geisler (Zeit.angew.Chem. ,1922. 35. 193) have obtained somewhat similar results with Oelsnitz gas coal, although the pyritic and sulphate sulphur present was not completely decomposed even in the high temperature coke. Their results are shown in the following table:—

	Coal (dry).	Semi-coke (Yield 74·2%).	Coke (Yield 63·5%).
Total Sulphur	1·78	1·66	1·58
Sulphur as pyrites	0·92	0·55	0·03
Sulphur as ferrous sulphide	—	0·05	0·46
Sulphur as sulphate	0·10	0·04	0·02
Organic sulphur	0·76	1·02	1·07

Many secondary reactions occur which are somewhat difficult to trace.

It would appear that it is chiefly the total amount of sulphur in the coal which is the determining factor governing the amount of sulphur in the coke, and whilst in some cases the sulphur may be much less than in the coal, in others, the actual percentage of sulphur in the coke may even exceed that in the coal. The following table due to Constam and Kolbe will emphasise this point (Gas J. 1909. 107. 696):—

Coal.	Percentage Sulphur in Coal.	Percentage Sulphur in Coke.
Nottingham, Bright Coal	1·10	0·83
Lancashire, Trencherbone	0·85	0·73
Nottingham, best hard	0·61	0·43
Kinneil	1·23	1·65
Durham, Low Main Seam	0·64	0·71
Durham, Hutton Seam	0·81	0·69
Yorkshire, Barnsley	0·61	0·43
Welsh, Nixon's Navigation	1·07	1·11

The above cokes were obtained by carbonisation in a retort.

With regard to pyrites, several distinct forms occur in coal, from lump pyrites, "brasses," etc., bright yellow in colour and crystalline, to fine dull powder scattered throughout the coal mass and not readily distinguishable from the coal itself, whilst thin veins, minute layers and other forms also exist. Whatever be the form, it is detrimental, and whilst lump pyrites can be removed in the coal washery, the other varieties present more difficulty and seriously detract from the value of a coal. Some kinds of pyrites readily oxidise in air, whilst others are scarcely affected even after years' exposure.

Of the organic sulphur, little is known. The compounds may be fairly simple or very complex in nature, a number of the complex molecules which go to form the coal substance each containing one or more sulphur atoms in their structure. Although it was proved by Muck in 1886 that organic sulphur did occur in coal, very little evidence has been put forward concerning the nature of these organic sulphur compounds. Part at least can be extracted by the use of organic solvents, and further, the "coal acids" obtained by Anderson and Roberts in 1898, by the action of nitric acid upon Scotch coals contained sulphur. A. R. Powell and S. W. Parr (Bull. 111 (1919), Eng.Expt.Stat., (University of Illinois) have divided the organic sulphur into resinic sulphur soluble in phenol, and humus sulphur, and concluded that the resinic and some of the humic sulphur is present in the coke.

Upon distillation, sulphur compounds appear in varying amounts in the three main products, viz., in the gas, in the liquid distillates (i.e., tar and ammoniacal liquor) and in the residual coke. The nature of these compounds as well as the relative amounts in the three products depend upon the temperature of carbonisation and on the nature of the coal used.

Sulphur in a coke detracts very materially from its commercial value, and the amount present is one of the chief factors in determining the suitability of a coke for metallurgical purposes. Since, upon combustion, the sulphur gives rise to sulphur dioxide, coke for domestic purposes must likewise be as free as possible from sulphur compounds. This also applies to all semi-cokes, low temperature cokes, smokeless fuels and briquettes intended for domestic fuel.

The gases from both high and low temperature carbonisation contain among other sulphur bodies sulphuretted hydrogen, whilst high temperature gas contains carbon disulphide in addition. Since these sulphur compounds, if left in the gas, would burn yielding poisonous sulphur dioxide which would escape into the room, coal gas, prior to distribution for domestic purposes must be purified as far as possible from all sulphur compounds. Hence the use of a coal of high sulphur content for making either smokeless fuels or ordinary coal gas is to be avoided.

It now remains to deal with the liquid products of distillation, which will be divided for convenience into

(*a*) Aqueous distillates.
(*b*) Tar.

The former contain inorganic substances such as sulphuretted hydrogen, ammonium sulphide and thiocyanate, sulphate and thiosulphate, and whilst the tar itself is also contaminated with these substances in entangled ammoniacal liquor, there are present many other sulphur compounds of an organic nature. These organic sulphur compounds in the tar are very difficult to eliminate, and since there are a large number with boiling points varying over a range of from 46° C. (carbon disulphide) upwards, the preparation of pure, sulphur-free substances from tar, e.g., pure benzene, is extremely costly. The chief of these organic sulphur compounds present are:—

Liquid.	Formula.	Boiling Point °C.
Carbon disulphide . .	CS_2	46
Thiophene . . .	C_4H_4S	84
Thiotclene . . .	C_5H_6S	113
Dimethylthiophenes . .	C_6H_8S	135-138

Owing to the proximity in boiling point of these sulphur compounds with the hydrocarbons present in the tar, fractional distillation does not completely effect their elimination. Fortunately, however, the removal of the last trace of sulphur is not often necessary.

CHAPTER III

HISTORY

Early patents on distillation—W. D. Scott Moncrieff and Parker's pioneering work—The Coalite Process—Rise of other processes—Glasgow Corporation and the Maclaurin Process—Demand for fuel oils and lubricants during the war—Institution of Petroleum Technologists committee's report—Ministry of Munitions' report on the production of fuel oil from home sources—The Fuel Research Board and the Fuel Research Station—The Pure Coal Briquette Process—Developments abroad—Conclusion.

A study of early patent literature is illuminating in considering the methods at present in vogue for carbonising coal. That raw coal is not satisfactory as a domestic fuel was recognised as early as 1656, Evelyn, in his diary, describing a project of Sir John Winter " of charring sea coale to burn out the sulphure, and render it sweete." Early patentees, however, seem to have concentrated on the production of tar and pitch from coal, rather than upon the production of a satisfactory domestic fuel, such tar and pitch being particularly applicable for the painting of the bottoms of ships and for the preserving of wood.

In 1685 (English Patent No. 247) Charles Corcelles patented " A New Way of Makeing Pitch or Tarr to preserve Shipps from being eaten by worms . . . the said Pitch or Tarr preserving all sorts of Wood from Corrupcŏn, and remaining upon it Six Times longer than the ordinary Sort, without Melting in the Sun, and for some time Resisting even Fire."

Mention appears to be first made of the direct distillation of coal by Talbot Edwards in 1716 (English Patent No. 405), who patented the making of pitch, tar and oil by " fluxing coal with fire only," whilst fifty years later we find that Christian Wilhelm Baron Von Haake (English Patent No.

1015, 1772) describes the distillation of coal in an iron cylinder, to obtain the " fluid matters issuing from the coal " and the production of vitriol, saltpetre and lamp-black by treatment of these fluid matters. Distillation of the tar produced by carbonisation was specifically patented by the Earl of Dundonald in 1781 (English Patent No. 1291), whilst in his method of carbonisation, the present Maclaurin Producer was surely forecasted, in so far as carbonisation of the coal was accomplished through heat generated in the mass of coal by the combustion of a portion of it, such combustion being controlled by the admission of air through ports into the apparatus.

A patent of particular interest, and of note in view of the comparatively recent proposal for the blending of coals prior to carbonisation, is that taken out by Alexander Cruckshanks in 1839 (English Patent No. 8141). Indeed, Cruckshanks appears to have been ahead of his time. He proposed the utilisation of the gas evolved from carbonaceous materials on distillation, in furnaces filled with brickwork under the stills, and suggested mixing a small proportion of coking coal with non-coking coal to render such non-coking coals available for the production of strong coherent coke. Further, his patent covers the introduction of steam into the still to effect the decomposition of the steam by the heated carbonaceous material, the use of the tar or oils obtained for heating purposes, i.e., as fuel oil, and the use of gas for heating buildings, in stoves in which brickwork or chequer work is placed.

Finally John Perkins of Manchester in 1853 (English Patent No. 307) patented the distillation at low temperatures of carbonaceous materials other than coal, such as shales, bass, and blaes, with the object of obtaining paraffin oil and oil containing paraffins, for lubricating purposes, and in the following year, James de Wolfe Sparr, of Birkenhead (English Patent No. 430, 1854), proposed the distillation of carbonaceous material including coal, primarily for the production of oil rather than gas, such distillation to be carried out under a high vacuum.

From the foregoing it is obvious that the ideas underlying many low temperature carbonisation processes of the present time are by no means new. The investigations carried on by these early workers, together with the genius and enthusiasm of men like Murdock, were responsible for the establishment of the gas industry. When it became known that the yield of gas per ton of coal carbonised was increased with higher temperatures of distillation, all hopes of carbonisation at low temperatures fell to the ground, since gas production was the main object of the industry, and the nature of the coke and tar was of secondary consideration. Furthermore, in the early days of the gas industry, tar was regarded as a necessary evil rather than as a product of considerable value, and the low temperature carbonisation of coal yielded a much greater quantity of tar per ton of coal carbonised than did distillation at higher temperatures.

In consequence, the low temperature carbonisation of coal became side-tracked in favour of high temperature carbonisation, and so it remained until W. D. Scott Moncrieff in 1880 proposed a scheme to alleviate the trouble consequent upon the pollution of the atmosphere with smoke.

Writing in "Nature" (1880, 23, 150), he described a process by which he proposed to make London a smokeless city. If the gas works, instead of obtaining 10,000 cubic feet of gas per ton of coal, only carried the distillation so far as to obtain one-third of this quantity, passing three times the amount of coal through the retorts, a richer gas, a higher yield of tar and a coke which would be suitable for domestic purposes would result. "The companies will have double the quantity of by-products they have at present in the shape of tar and ammonia liquors; the community will have 24-candle gas instead of 16-candle gas; the fuel resulting from the process will light readily and it will make a cheerful fire which gives out 20 per cent. more heat than common coal . . . it lights easily, it gives off no smoke, it makes a cheerful fire. . . ."

Although Moncrieff's scheme did not fructify for reasons which are discussed elsewhere, yet the prospect of producing a smokeless fuel and a pure atmosphere by new methods of carbonisation was opened out. In the same year, Thomas Parker, the inventor of Coalite, obtained a medal at the Smoke Abatement Exhibition for one of the first slow combustion stoves introduced.

Ten years later, in 1890, Parker took out his first patent (English Patent 67, 1890), for the production of a smokeless fuel by passing steam, water gas or coal gas, superheated to a temperature of 600-650° C. through a mass of coal in a retort, but it was not until 1906 that he took out his master patents (14,365 and 17,347) for the manufacture of Coalite, and a company was formed to work the process. Patent rights were also secured in other countries, the patentee making the following claims for his invention :—

(1) An improved hard and smokeless fuel prepared from bituminous coal by a process of partial destructive distillation carried on substantially as hereinbefore described (i.e., by heating coal in shallow layers about six inches deep in closed retorts for about six hours).

(2) A process for the preparation of a hard and smokeless fuel from bituminous coal, consisting in subjecting the coal to partial destructive distillation so that the whole mass of the coal is maintained at the temperature of about 800° F. until the illuminating gases cease to be evolved, and then stopping the distillation and quenching the fuel.

Prior to quenching, the fuel is treated with steam.

With the establishment of this company, the low temperature carbonisation of coal made a definite step forward into the realm of commercialism, for in 1907 the Coalite Company applied to Parliament to obtain authority to erect premises at Barking for the purpose of supplying West and East Ham, Barking Town and East Woolwich with gas.

From this date onwards, the affairs of the company were subject to excessive fluctuations and the high hopes which the company entertained were not realised. In 1909 a Coalite plant was erected at Plymouth Gas Works consisting of three units, each 52 ft. long by 13 ft. wide, the retorts each 9 ft. in length, being tubular in shape, 4·5 ins. in diameter at the top, expanding to 5·25 ins. in diameter at the bottom to facilitate the removal of the coke.

The type of retort employed has varied considerably, but the retort used by the present Coalite Company (Low Temperature Carbonisation Ltd., Barnsley) is entirely different in construction from those originally designed (see p. 87).

The Coalite Company can be regarded as the pioneer of low temperature carbonisation processes, and when finally success is attained, and a smokeless fuel used to the exclusion of raw coal, with the accruing advantages possessed by such a fuel, Parker should surely figure amongst those who, having dreamed dreams and seen visions, have opened the way to a healthier and more contented community.

As might be expected, it was not long after Parker's patents of 1906 that other processes of low temperature carbonisation were put forward, one of the foremost amongst them being that of the Premier Tarless Fuel Syndicate, who completed plant at Battersea in July, 1910, to work the process covered by patents 7,732 of 1906, and 20,237 of 1909 taken out by W. Spiers Simpson, whilst in 1913, the proprietors of the Del Monte patents issued their prospectus for capitalising Oil and Carbon Products Ltd.

Details of several processes advocated during this period are given in a later chapter, but none of them proved successful on a large commercial scale, due largely to the fact that the fundamentals of coal carbonisation at low temperatures were not recognised. Many inventors regarded their processes as destined ultimately to supersede carbonisation at high temperature, resulting in much controversy between the prospective and the established industries.

A perusal of the Gas Journal issued during this time shows the disrepute which the advocates of low temperature carbonisation gained, owing largely to the excessive claims which they made and which were never substantiated in large scale plant. The action of the Glasgow Corporation Gas Committee, however, shows a striking contrast to the attitude taken up by other branches of the gas industry.

The possibility of utilising the coke from their retorts in the ordinary domestic fireplace induced the Glasgow Corporation in 1909 to appoint a sub-committee to investigate any processes yielding a fuel suitable for domestic hearths, and experiments were made with Coalexld, produced by mixing certain chemicals with the coal prior to its introduction into the retorts. The results, however, were far from promising, and in 1916 the sub-committee selected the process proposed and patented by Maclaurin (English Patent 24,426 of 1913), with the result that an experimental plant was erected at the Port Dundas Electricity Station of the Glasgow Corporation under the supervision of the patentee.

The following extracts from a letter in the *Glasgow Herald* of December 31st, 1921, in reply to a criticism of the Glasgow Corporation on its lack of interest in " Smokeless Fuel " serves to illustrate the establishment and progress of the Maclaurin Process in Glasgow.

" . . . Why is it that so many of our citizens are so ready to impute blame to the Corporation in connection with almost every subject? Members of the Corporation have not been asleep over this matter.

" In 1909 I proposed a motion in the Gas Committee on this subject. The minute of December 24th, 1909, reads:

" ' The Committee, on the motion of Councillor W. B. Smith, agreed to recommend that it be remitted to the following sub-committee, viz., Baillie Kirkland, and Councillors Moir, Montgomery, M'Lean, Smith (Convener), and James Young, along with the general manager, to inquire into and report on any process of gas making that will produce a form of coal residue that may be available for use in ordinary domestic grates.

" . . . On August 26th, 1910, it is minuted that this sub-committee instructed the Gas Manager to make some experiments with steam quenched coke and another substance. Nothing resulted from this.

" On February 24th, 1911, I brought before the Gas Committee a suggestion that they employ Mr T. Parker, who invented coalite, to design and instal a plant in our gas works to make a fuel, but on the advice of the Engineer they declined to consider the proposal.

" On March 24th, 1914, on my suggestion the Electricity Committee appointed a sub-committee to consider the question of using gas to fire the boilers at the generating stations, and the extraction of the tar, etc., in the coal carbonised, and the sub-committee remitted the matter to a special sub-committee consisting of Baillies Smith (Convener), Morton, Nichol, Kennedy and Hannay, and Councillors Mollison, Sadler, P. G. Stewart and Willcock for consideration and report.

" A few months later, having considered the various processes that make smokeless fuel, we instructed the Town Clerk to write to everyone in Britain who was known to have any processes for producing smokeless fuel, asking them the probable cost of erecting an experimental plant to test each process, and as to the patent royalties should the Corporation adopt one.

" After examining all the processes put before us, we decided that the process patented by R. Maclaurin seemed the most likely for our purpose. On May 22nd, 1914, the sub-committee decided that the offer of Mr. Maclaurin to erect the plant referred to in the minute of this special sub-committee of the 21st ult. be accepted, and that it be remitted to this special sub-committee (*a*) to negotiate with Mr. Maclaurin as to the terms and conditions which he is prepared to grant to the Corporation in the event of them desiring to erect installations of his plant at the gas works: and (*b*) to see the work in connection with the experiments now proposed to be made carried out.

" This was approved by the Gas Committee and the Corporation. On March 3rd, 1915, the Electricity Department decided to take a share in this experiment and use the gas for firing their boilers, and the erection of the plant to carbonise 20 tons of coal per day was started in Port Dundas generating station.

" Experiments went on until war conditions made it impossible to continue them there, as neither coal nor labour could be got, and later, this plant was taken down and removed to Grangemouth, where it was re-erected with several alterations and improvements that trials had shown to be necessary.

" All this time experiments continued, and a great deal of chemical research was being made by the inventor and his chemists into the by-products produced by the processes, which are quite different from those in the ordinary processes of gas making.

" We are now at the culmination of these years of work, and the results have been reported to the special sub-committee, who are putting it before the Gas Committee, and through them to the Corporation, and the results will be given very shortly.

" It is now open to the various gas undertakings and coal producers to adopt the process and put a smokeless fuel on the market in quantities at a reasonable price.

" I think your readers will admit that the Corporation deserve some credit for all this work.—I am, etc.,

" William B. Smith."

In a lecture before the Royal Society of Arts (J. Roy. Soc. Arts, 1913, 62, 103), Sir Boverton Redwood in 1913 drew attention to the growing demand for oils for use as motor spirit, for steam raising, and as fuel in engines of the Diesel and semi-Diesel type, suggesting at the same time the possibilities of their preparaton from coal by a distillation process. Furthermore, in view of the high thermal efficiency of engines of the Diesel type and of the fact that fuel oil instead of coal was being used for marine work, especially for war vessels, it was expedient that England should not be dependent upon foreign countries for her supplies of fuel oil. In 1901, the world's output of petroleum amounted to 22,000,000 metric tons, whilst in 1911, it had more than doubled, reaching 46,500,000 metric tons, or an increase of from 2·8 to 4·3 per cent. of the world's coal output. In the latter year, the United States were responsible for approximately 63 per cent. of the petroleum output of the world, Russia contributing 20 per cent., Mexico 4·7 per cent., whilst the remainder, approximately 12·3 per cent., came from other countries, none being supplied by Great Britain, i.e., excluding the shale oil produced in Scotland.

With the advent of the War, the question of liquid fuels and lubricants became a matter of such vital importance to England that the problem was taken in hand by the

Ministry of Munitions. The chief points at issue were briefly as follows:—

1. The economic use of our coal supplies.
2. The demand for benzene and toluene for the manufacture of explosives and other munitions of war.
3. The sudden increasing demand for fuel oils of various kinds consisting of:
    (*a*) Motor spirit.
    (*b*) Oil for use in Diesel engines.
    (*c*) Fuel oil for the Navy.
4. The manufacture of lubricants for all purposes.

Attention was concentrated upon the carbonisation of coal and kindred substances at low and high temperatures, and the difficulties encountered in low temperature carbonisation were echoed in a statement made in Parliament by Dr. Addison in October, 1916, concerning the question of subjecting coals of high volatile matter content to low temperature distillation, as carried out in Germany. He stated that the matter was receiving consideration, but its advantages with regard to the manufacture of material for explosives were problematical, whilst the coke from cannel and material of a like nature was of little use.

The question of the utilisation of coals, cannels and shales as a raw material for manufacturing liquid fuels became of such importance that the Institute of Petroleum Technologists in February, 1918, appointed a committee " to enquire into the possibility of employing cannel coal and allied substances in Great Britain as a source of supply of motor spirit, fuel oil and other products, and to formulate a scheme for the utilising of these minerals in the manner indicated," whilst in March of the same year, the Minister of Munitions, in agreement with the Secretary of State for the Colonies, appointed a committee, with the Marquess of Crewe at its head, " to enquire into matters concerning the production of fuel oil from home sources, and to consider the report rendered by the Petroleum Research Department of the Ministry of Munitions under the directorship of Sir

Boverton Redwood, on the production of fuel oil from home sources. . . ."

The Institution of Petroleum Technologists made their full report in July, 1918, followed a few days later by the Marquess of Crewe's report. In view of the fact that the reports were drawn up by what might be termed two independent bodies of specialists, they constitute important steps in the progress of low temperature carbonisation, and are considered of such a nature that extracts from the two reports are given in verbatim below. It must be borne in mind that cannel coal and similar material yields on distillation a residue not suitable for immediate use as a smokeless fuel, thus differing considerably from the product obtained by distilling bituminous coals at low temperatures. In the former case, the process is designed to produce liquid fuels and ammonium sulphate, whilst the economical aspect of the process is different in so far that the coke produced by the low temperature carbonisation of bituminous coals constitutes the most valuable by-product of the industry.

Extracts from the Report of the Institution of Petroleum Technologists

1. The possibility of obtaining oil in quantity from the low temperature distillation of cannel coal and its cognates has been considered from two points of view—namely:—

(1) As an immediate war measure, having in view the production of motor spirit and fuel oil for the services.
(2) As a permanent commercial undertaking and a measure of reconstruction.

2. Sufficient evidence having been obtained from colliery proprietors and others to justify the conclusion that a very large amount of retortable material can be obtained for the production of oil in Great Britain, the Committee have decided to issue this interim report.

3. The raw material in sight divides itself into three classes;—

(*a*) Non-caking material with a high yield of oil giving a residue of low value as household and steam-raising fuel, but of considerable value for producer gas and other purposes.

(*b*) Caking material and non-caking material with a smaller yield of oil than (*a*) but affording a residue of great value for domestic and industrial fuel.

(*c*) Material of variety intermediate between (*a*) and (*b*).

4. As a result of tests carried out by various processes, it has been established that a yield of between 15 and 80 gals. of crude oil per ton can be obtained from material existing in the British Isles. This crude oil can be refined to give at least 8 per cent. of spirit and 40 to 50 per cent. of fuel oil.

5. The Committee are satisfied that at least 10,000 tons per day of retortable material could be economically assembled for treatment, provided the necessary facilities were given by the Government and the requisite labour were available. At an average of 30 gals. of oil per ton, this would yield 300,000 gals. of crude oil a day, or upwards of 400,000 tons a year.

6. Much of this material has hitherto been mined but not raised, or if raised, has been thrown upon the soil heaps or returned to the underground working. If the substitution of the shovel for the fork, so strongly demanded by the miners, were made obligatory by Government order, still more material would be sent up and wasted. If, however, the recommendations of this Committee be adopted, and retorts erected, the increased supply of material will be utilised, and the colliery owner will be able to pay the miner for the extra tonnage brought to bank.

7. The development of the industry as a permanent commercial undertaking depends upon the utilisation of the by-products and residues.

8. The efficient utilisation, by means of low temperature distillation, of the heat energy of the raw materials employed will make available valuable constituents which now go to waste, and thus tend to relieve the shortage of fuel for domestic and industrial purposes.

9. (*a*) The residues obtained from caking material will provide a considerable supply of clean fuel without smoke, and of high calorific value.

(*b*) The residues obtained from a non-caking material, high in ash, can be utilised in a producer for the production of power gas and sulphate of ammonia. The quantity of gas must depend on the relative proportions of carbon and ash in the residue, and, consequently, no generalisation as to the yield of gas is possible.

(*c*) The residues obtained from a non-caking coal low in ash can be utilised in the manufacture of briquettes.

10. It must also be borne in mind that the utilisation of the large quantities of residues obtainable from the treatment of non-caking material should greatly facilitate the schemes for generating cheap electrical power which have been the subject of consideration by the Electrical Power Supply Committee of the Board of Trade and the Coal Conservation Sub-Committee of the Ministry of Reconstruction.

11. The technical advisers of the Committee have carefully investigated several types of retort, and also have had submitted to them many suggestions by inventors and others which hold forth considerable promise. As the materials to be treated vary widely in natural characteristics and in their behaviour within the retort, it is apparent that no one type of retort can treat to the best advantage all classes of material. There is, however, every reason to believe that certain retorts which have been under consideration will treat either caking or non-caking bituminous material so as to give a satisfactory throughput. There are in existence retorts which will successfully recover the maximum oil content.

12. The Committee have not overlooked the question of the labour which will be required; but they desire to emphasise the fact that the establishment of an industry for the low temperature distillation of cannel coal and its cognates will afford many openings for the employment of unskilled surface labour.

13. The Committee regard with apprehension the situation as to the supply of fuel oil and motor spirit, and the long delay in taking action to develop home supplies. They

therefore strongly urge the adoption of the following recommendations:—

(1) That the War Cabinet should be invited to lay down a definite policy for the guidance of the Departments as to the relative value and importance at the present time of oil and coal, the provision of the necessary labour, raw materials, and transport.

(2) That the Government should afford all necessary facilities to those who are prepared to find the capital, and take the risk, for the erection at suitable centres of plant for the treatment on a commercial basis of the material known to exist.

(3) That an experimental station be established forthwith, so that retorts of any design, provisionally approved by the Institution of Petroleum Technologists, can be erected and tried out, and material tested with a view to ascertaining its character, oil yield, and residual values.

(4) That such experimental station shall be maintained by, and at the expense of the Government; or, alternatively,

(5) That the Government shall afford all necessary and reasonable facilities to the Institution of Petroleum Technologists for the erection of a testing station of their own.

Extracts from the Report of a Committee appointed by the Minister of Munitions respecting the Production of Fuel Oil from Home Sources

Since the bulk of the enquiries detailed in this report deal with the production of fuel oil chiefly from cannel and similar substances, it is only proposed to give a few of the sections which either are of general interest as bearing upon low temperature carbonisation in all its phases, or which make special mention of the use of bituminous coal for the production of fuel oil and smokeless fuel.

Extracts from the Report

1. Low temperature carbonisation, except in its application in the Scottish Shale Industry, has not yet been proved industrially, and consequently the erection of large units of retorts to carbonise cannel coal and kindred substances could not be justified until success had been demonstrated on a reasonably large scale. . . .

2. A committee had been appointed in 1917 to investigate the advantages and disadvantages of three types of low temperature retorts; comparative tests were made, and the results appeared to be in favour of the form of vertical retort used in the Scottish Shale Oil Industry. In view, however, of the strong representations of the Petroleum Research Department in favour of the installation of the Chiswick type of retort for the carbonisation of cannel coal and kindred substances, the Production Department decided to instal a battery of thirty of these retorts at Nottingham, so that practical experience of their working on an industrial scale might be obtained under similar conditions to those prevailing at the Nottingham Gas Works, where cannel coal is being dealt with in the existing vertical gas works retorts which have been adapted for the purpose. . . .

3. . . . A sample of the oil has been tested at the Naval Fuel Depot at Haslar, and it has been found to be suitable for utilisation as fuel for the Navy if mixed in certain proportions with petroleum taken from stock. Certain physical treatment is necessary, but refining by distillation or chemical treatment is not required.

4. . . . other sources of supply appear to be:—

(*a*) Boring for oil in Great Britain.
(*b*) Further development of the Scottish Shale Oil Industry.
(*c*) The utilisation of dehydrated tar by the employment of suitable solvents.
(*d*) A great extension of the carbonisation of raw coal as a preliminary to its use for industrial and domestic purposes. As the greater part of the coal consumed in Great Britain is used in the raw state, there is obviously wide scope in this direction for developments on a

> really important scale. For every 20 million tons of coal carbonised, from 1 to 1·25 million tons of fuel oil might be obtained. The Fuel Research Board of the Department of Scientific and Industrial Research is now developing a comprehensive enquiry into the technical and economic possibilities of such a revolution in the preparation and use of fuel for industrial and domestic purposes.

In 1917, a Board of Fuel Research was appointed by the Committee of the Privy Council for Scientific and Industrial Research on the recommendation of their Advisory Committee.

Sir George Beilby, F.R.S., consented to act as director of the Board, assisted by the Hon. Sir Charles Parsons, K.C.B., F.R.S., Mr. Richard Threlfall, F.R.S., and Sir Richard Redmayne; Professor W. A. Bone, F.R.S., being retained as consultant.

Two main lines of research were to be pursued; first, the survey and correlation of the coal seams in the various mining areas, by means of chemical and physical tests, and secondly, an investigation of the practical problems awaiting solution if the raw coal at present consumed is to be replaced by the various products obtainable from coal by carbonisation and gasification.

The erection of a Fuel Research Station was subsequently undertaken at East Greenwich, and was completed in 1919, commencing active research in August of that year.

It was erected on a very generous scale, units of plant on an industrial scale being installed, together with laboratories completely equipped with the most modern types of apparatus (Report of The Fuel Research Board for the years 1918, 1919, H.M. Stationery Office).

The carbonisation of coal at low temperatures figures largely in the second line of research mentioned above, and the value of the work which has been carried out at East Greenwich, since the inception of the Fuel Research Station, towards the placing of the new industry upon a sound economic basis cannot be estimated.

In 1916, a committee was appointed by the British

Association for the Investigation of Fuel Economy, the Utilisation of Coal, and Smoke Prevention, and this committee has given very valuable assistance in the solving of these problems which are of such vital moment to the nation as a whole.

At the present time, rapid developments are taking place, and the Pure Coal Briquette Process, of which details are given later, makes claims which, if substantiated, bid fair to revolutionise our conception of carbonisation, and its future will be watched with the greatest interest by many sections of the community.

Development in Other Countries

England is by no means the only country in which the question of the low temperature carbonisation of coal and allied materials is being investigated, and although much of this work, especially in Canada and Germany, is connected with the use of material other than bituminous coal, namely lignites, the general process of treatment is very similar. In America, the first large plant to be erected was for the purpose of working the process patented by C. H. Smith, for the manufacture of a smokeless fuel known as Carbocoal. The first plant was completed in 1918 at Irvington, New Jersey, whilst a much larger plant at Clinchfield, Va., with a capacity of 550 tons of smokeless fuel per day, started producing in July, 1920.

The Clinchfield plant is certainly the largest scale plant yet erected for the production of smokeless fuel. Carbocoal cannot, however, be regarded as a fuel suitable for the open domestic grate, resembling anthracite in properties.

Many American processes are still in embryo, not having yet been proved on an industrial scale, whilst the development of other processes promises in the near future. At the same time, such development is aided by the very able and complete research work which is carried out on what might be termed a fairly large experimental scale at institutions such as the Engineering Experimental Station, University of Illinois, Urbana, Illinois, the U.S. Bureau of Mines, and the Mellon Institute of Industrial Research. The extent of such research work can be gauged by a perusal of the publications of the various investigators at these Institutions. American processes, in course of development, are described in a later portion of this book (p. 128 *seq.*).

In Canada, work on low temperature carbonisation appears to have developed in the course of work upon the low grade lignite deposits of southern Saskatchewan, and elsewhere. In 1918, by an Order-in-Council of the Dominion of Canada, supplemented by a financial agreement with the Manitoba and Saskatchewan Governments, the Lignite Utilisation Board of Canada was created, to formulate means whereby low-grade lignite deposits could be converted into domestic fuel. Preliminary investigations were carried out at the Fuel Testing Station, Mines Branch, Dept. of Mines, Ottawa, Canada, and subsequently a semi-commercial scale plant was erected in Ottawa.

Stansfield (J.Ind.Eng.Chem., 1921. 13. 17) states that a plant is now being erected by the Board, near Bienfait, Saskatchewan, capable of carbonising 200 tons of raw lignite per day. Briquettes produced by the Lignite Utilisation Board appear to be fairly satisfactory, but a description of the carbonisation of lignite is outside the scope of this book.

Owing largely to the scarcity of fuel oil and lubricants during the war, research work upon the low temperature carbonisation of coal, and particularly of brown coal, has made great progress in Germany. In that country, perhaps more than elsewhere, the constitution of low temperature tars has been studied, and the work of Fischer and Gluud and their contemporaries has placed Germany in the forefront with regard to the economic utilisation of such tar.

It has not been possible to detail the course of the scientific investigation of problems arising in the low temperature distillation of coal and allied materials, but on subsequent pages the salient features of the more recent research work are incorporated in the text.

For fuller information the reader is referred to publications given in the bibliography (p. 227).

Viewing the situation as a whole, the solution of the problems associated with low temperature carbonisation is gradually being attained, and, since the days of Parker, fairly constant progress has been made both in the designing of suitable plant and in the study of the fundamental principles underlying the problem.

The War period saw a distinct impetus given to investigations and experiments, arising mainly through the realisation of the dependency of certain countries upon foreign supplies of fuel oils and lubricants. Since the war, whilst the possibilities with regard to oil supplies have not been overlooked, the general tendency has been towards the production of a smokeless fuel suitable for every purpose to which coal in its natural state is applied, and a general awakening is manifest with regard to the present wasteful methods of using coal, and the injurious effects of smoke.

Articles in the daily press, increased propaganda of "Smoke Abatement" organisations, and the activities of municipal authorities, as well as the increasing interest of those directly concerned in our coal supplies, is evidence of such awakening, and the gradual education of the public appears to be moving hand in hand with the progress which is finally to establish the all-important industry of the carbonisation of coal at low temperatures.

CHAPTER IV

LOW TEMPERATURE CARBONISATION COKE

NECESSARY CHARACTERISTICS OF LOW TEMPERATURE CARBONISATION COKE—DIFFICULTIES ENCOUNTERED IN ITS PREPARATION—EXPANSION OF COAL ON HEATING—THE MEANS OF COUNTERACTING THIS—THE CONDUCTIVITY OF COAL—COMPOSITION OF SEMI-COKES FROM VARIOUS PROCESSES—THE VOLATILE ORGANIC MATTER IN COAL AND COKE—MOISTURE CONTENT OF SEMI-COKES—THEIR HEATING VALUE—USES AS DOMESTIC FUEL—PRODUCER FUEL—FOR STEAM RAISING AND GENERAL INDUSTRIAL PURPOSES.

In order to satisfy the requirements of a smokeless fuel, particularly one which will be suitable for domestic use, any low temperature carbonisation coke must possess certain characteristics. Essentially these are as follows:—

1. The coke must readily ignite in order that no difficulty may be experienced in lighting a fire in the ordinary domestic appliances.

2. The coke must be reasonably hard and compact in order to withstand breakage in transport from the producer to the consumer and not be susceptible to excessive weathering, so that it may be stored for a time without depreciation.

3. The coke must not contain more than a certain proportion of incombustible matter, consisting of ash and moisture, having a maximum limit of, say, 10 per cent. ash and 5 per cent. moisture, possessing, at the same time, a reasonable calorific value.

4. The coke must be uniform in texture and be moderately clean to handle.

True low temperature carbonisation coke will satisfy the requirements of a smokeless fuel subject to the above conditions.

The bad heat conductivity of coal and its expansion on heating are mainly responsible for the difficulties encountered in producing, on an industrial scale, a low temperature coke which will fulfil all the conditions mentioned above.

The Expansion of Coal

The expansion which occurs in the case of many coals when subjected to heat is dependent, to a large extent, on the temperature to which the coal is heated and the rate of heating. The melting of the binding material in the coal takes place at about 350 to 450° C., varying with the nature of the coal, the " binder " then fusing and cementing the mass. The continued application of heat decomposes the binder with the subsequent expansion of the coal. J. Roberts, in a paper on " The Carbonisation of Coal at Low Temperatures " (Trans.Inst.Min.Eng. 1921, 62, 9) illustrated this binding and decomposition by heating a mass of coal (200 gms.) in a fireclay crucible over a Bunsen burner, until a thermometer placed in the centre of the mass showed a temperature of 360° C., at which stage the crucible was allowed to cool. On removing that portion of the coal which had not fused and examining that which was coherent, two distinct zones were discernible: (*a*) a fused zone which was compact and which travelled in advance of a decomposition zone (*b*), which was highly porous. In this zone, the already fused binding material had undergone decomposition, resulting in the production of a highly cellular structure, causing the mass to swell considerably. Surrounding this zone, due to continued and greater heating, the mass contained a further zone of semi-coke which showed a less swollen structure than that of the decomposition zone, whilst the outside layer formed the final zone corresponding to the high temperature coke zone, which exhibited a still denser structure.

The mass showed the definite course of the physical structures through which coal passed on being heated to a final stage of high temperature coke. Consequent upon the swelling of the mass due to the decomposition of the binding material, such swelling has to be provided for in any process for the production of semi-coke or low temperature carbonisation coke. This swelling is particularly excessive in coals possessing a large amount of binding material, as is the case with certain bituminous coals specially noted for this peculiar property and used extensively in the manufacture of metallurgical coke. Roberts could not trace any definite relationship between the volatile matter in a coal and the swelling power of the coal, except in cases where the coals came from limited areas, as for example, the South Wales Coalfield, in which progressive anthracitisation has taken place from east to west, resulting in a loss of volatile matter and in the destruction or partial destruction of the binding material. The author then proceeded to enumerate methods by which such swelling may be overcome. By mixing a comparatively inert material, such as coke, with a highly swelling coal, it is possible to use up any excessive binding material present in the coal. Parr and Olin (Bulletin No. 39, May 31st, 1915, Eng.Expt.Stat., University of Illinois), studying the coking of coal at low temperatures, state that "Strangely enough, the abundance of coking material which coals of the western types possess, is the cause of their inferiority in the matter of making dense, hard cokes; for with the decomposition of the resinic bodies and the deposition of the cementing carbon, there occurs, at the same time, an evolution of large quantities of gases which inflate the pasty mass and make the resulting coke more or less light and spongy. Indeed, certain Vermilion County Coals, after being heated under conditions which allow for expansion, present the appearance of hardened froth, because of the excessive development of cell structure in the coke." To overcome such difficulties, the authors of the above bulletin present two possible remedies:

1. The compression of the coal during carbonisation.
2. The addition of inert coke dust to act in the capacity of an absorbent for the excessive binding material present.

By the addition of such inert matter, consisting of a mixture of various semi-cokes of a fineness of from 40-60 mesh sieve, it was found possible to produce hard, firm cokes from the Vermilion County Coal, the dilution with such inert matter being of the order of 100 per cent. It is also stated that by this treatment, the texture of the resulting semi-coke was made firmer and the density increased.

A study of this phenomenon has been made by Sinnatt and Grounds (J.Soc.Chem.Ind. 1920, 39, 83T, and Bulletin No. 8 Lancashire and Cheshire Coal Research Association); indeed, it was applied as early as 1859, when M. Joseph Souquière of Paris took out a patent for a New and Improved Process for Distilling Coal (English Patent No. 1,091 of 1859) in which he agglomerates coal and coke prior to carbonisation, claiming at the same time that such a mixture is more rapidly coked. At the present time, Low Temperature Carbonisation Ltd., at Barnsley, in producing coalite in the modern plant, mix coals of varying coking powers, thus obtaining a product which has a definite coking power.

Difficulty encountered due to the Bad Heat Conductivity of the Coal

Coal is a particularly bad conductor of heat, and even with the high temperatures obtaining in gas works and coke-oven practice (1000-1200° C.), several hours must elapse before the centre of a coal charge shows any corresponding increase in temperature. Owing to this fact, it becomes difficult in low temperature carbonisation processes to obtain a sufficiently rapid heating of the coal charge in view of the low temperature to which the coal must be subjected, viz., about 550° C.

In one of the earliest attempts to produce smokeless fuel, Scott Moncrieff failed to recognise this fundamental, endeavouring to make use of the ordinary gas works plant, when, instead of producing a semi-coke, a mass of material was obtained which consisted of a central core of coal, surrounded by a sticky layer, and finally by an annulus of coke which graded from material of a highly cellular nature—the true low temperature coke—to a very hard, compact coke, the product of high temperature carbonisation, the whole conglomerate being entirely useless for the purpose for which it was intended.

Whilst few definite measurements appear to have been made of the conductivity of coal at different temperatures, the difficulty here set forth is enhanced by the fact that the formation of semi-coke is preceded in the decomposition of the coal by a phase in which the coal is in a plastic condition, which further materially effects the passage of heat into the coal mass. Following upon the failure of Moncrieff's method, a radical change in the method of heating was made by Parker, who, recognising this difficulty of low conductivity, designed retorts which were of very small cross section.

Subsequent investigators have either followed the lead of Parker in employing retorts of a small cross section, or have endeavoured to overcome the difficulty of heat transmission by allowing a heat conveyor such as producer gas, or superheated steam, to come into intimate contact with the coal to be carbonised. Roberts (*loc. cit.*) gives heat transmission curves showing the effect of the addition of an inert coke to a coal prior to carbonisation. Using 200 gms. of a Welsh coal, and heating it in a fireclay crucible, suitably insulated from draughts, he states that with coal alone, 57½ minutes elapsed before the centre of the charge reached a temperature of 360° C., at which temperature the experiment was stopped, whereas with a mixture of the same coal and 20 per cent. of coke breeze, the time taken was 45½ minutes; whilst with 30 per cent. of coke breeze, the temperature was reached in 31 minutes. This increased conductivity is not solely due to the better conductivity of the coke added, but also to the fact that the decomposition zone is destroyed as a result of the utilisation of the surplus cementing material as a binder for the inert coke.

Parr and Olin (Bulletins Nos. 60 and 79, Eng.Expt.Stat., University of Illinois) also suggest the use of such inert material. As this inert material must be of a fairly small size and at the same time be thoroughly incorporated with the coal to be carbonised, the application of this principle industrially presents some difficulties, whilst at the same time, adding to the cost of any process in which it may be employed. The practical outcome appears to be that employed by Low Temperature Carbonisation Ltd., Barnsley (see Coalite Process, p. 87), in which an ungraded non-caking slack is compounded with an ungraded caking slack to produce a mixture of suitable caking power. Reference is made elsewhere (pp. 81-84) to the practical difficulties encountered in efficient blending. The most efficient blending obtains in the Pure Coal Briquette Process, in which the non-caking coal, or coke obtained from the process, is thoroughly incorporated with the coal during pulverisation to a comparatively fine state of division. Illingworth (English Patent 161,104, 1921) has suggested an alternative means of overcoming excessive swelling during carbonisation (p. 142).

Composition of Low Temperature Carbonisation Cokes

Although low temperature carbonisation processes have not, up to the present time, succeeded in the production of semi-coke in bulk, that is on a scale comparable with the production of coke in coke ovens and gas works, as for example with units capable of producing over 500 tons per day, yet many plants are in existence which produce small quantities of excellent smokeless fuel. In consequence the nature of such smokeless fuel or semi-coke is well known.

Analyses of low temperature cokes produced at H.M. Fuel Research Station, East Greenwich (Dr. Fishenden, Fuel Research Board Technical Paper No. 3, 1921) are given below together with analyses of semi-cokes obtained from various processes.

Low Temperature Cokes from H.M. Fuel Research Station, E. Greenwich

	Percentage Composition			
	No. 1.	No. 2.	No. 3.	No. 4.
Moisture	2·6	2·6	3·1	2·7
Ash	12·8	9·0	9·8	8·8
Volatile Matter	14·1	13·0	12·6	11·5
Volatile Organic Matter	11·6	10·4	9·5	8·8
Coke	85·9	87·0	87·4	88·5
Fixed Carbon	73·1	78·0	77·6	79·6
Sulphur	—	—	0·9	1·1
Calorific Value in B.Th.U's. per lb.	11,900	12,400	12,200	12,900

Percentage Composition.								
Type of Low Temperature Carbonisation Coke.	Coke from Derbyshire Coal containing Ash, 14·85 H_2O, 5·30 Freeman Multiple Retort.	Coke from Bituminous Slack. Ash, 12·4 H_2O, 2·8 L. M. N. Rotary Retort.	Coke from Franklin Co. Coal. Ash, 7·38 H_2O, 6·84	Carbocoal.	Coalite.	Hargreaves Coke.	Coke from Maclaurin Process (Cadder Coking Coal) Ash, 6·19 H_2O, 10·40	Coke from Pure Coal Briquette. Process for Metallurgical Work.
Moisture . . .	...	1·90	0·40	2·03	...	0·60	...	3·5
Ash	16·35	15·90	9·28	15·66	6·4	10·70	8·52	10·6
Volatile Matter . . .	...	13·40	27·00	5·94	...	7·80	...	4·8
Volatile Organic Matter .	10·39	11·50	26·60	3·91	10·0	7·20	4·77	1·3
Coke	89·61	86·60	73·00	94·06	90·0	92·20	...	95·2
Fixed Carbon . . .	73·26	70·70	63·72	78·40	83·6	81·50	86·71	84·6
Sulphur	...	1·70	1·21	...	...	...	...	1·9
Calorific Value B.Th.U's. per lb.	...	12,550	13,446	11,570	...	13 180	...	...
Source	N. H. Freeman	F. D. Marshall	Parr and Olin. Bull. 60. Eng. Expt. Station, Illinois.	F. S. Sinnatt. Journal Roy. San. Inst. Vol. XLII. No. 1 (1921)	Engineering, 1921, 112, 598.	F. S. Sinnatt. Journal Roy. San. Inst. Vol. XLII. No. 1 (1921)	Maclaurin. J. Soc. Chem. Ind. 1917, 36, 620.	E. C. Evans

Volatile Organic Matter

It will be noted that whereas ordinary gas works coke contains a maximum of about 2 per cent. of volatile organic matter, low temperature carbonisation cokes show considerably higher contents varying generally, due to the conditions under which they are produced, from 10 per cent. to 20 per cent. In the case of Carbocoal and the coke produced by the Pure Coal Briquette Process, the products contain a smaller percentage of volatile matter than usual. The subsequent remarks, however, apply, within limits, to Carbocoal and Pure Coal Briquette Coke. Parr and Olin, reviewing the presence of this volatile organic matter in low temperature carbonisation cokes, and the smokeless nature of such coke, illustrate it by a consideration of the reactions which take place when coal is burned under normal conditions (Bulletin 60, Eng.Expt.Stat., University of Illinois). When coal is thrown upon a fire, the temperature is lowered for a time, owing to the absorption of heat for the volatilisation of the moisture in the coal, and for the raising of the temperature of the coal substance to a point at which the decomposition reactions become exothermic, which temperature, according to Hollings and Cobb (Gas J., 1914, 126, 923), using Monckton coal, is 410° C. Beyond this temperature Hollings and Cobb state that exothermic and endothermic reactions take place—possibly, at certain temperatures, simultaneously, but it is only with reactions up to this temperature with which we are concerned. During the depression of the general temperature, there are distilled from the coal, substances which are volatile at this temperature. This volatile matter consists of the bulk of the heavy hydrocarbons, which contain a high percentage of carbon, being higher members of the paraffin, naphthene and ethylene series (C_nH_{2n+2}; C_nH_{2n}). For example, the carbon percentages of methane, ethane, and propane of the C_nH_{2n+2} series are respectively, CH_4, 75 per cent., C_2H_6, 80 per cent., C_3H_8, 81·8 per cent. and similarly with the naphthene and ethylene series C_nH_{2n}, the first member of each series having a carbon content of 92·92 per cent. Further, these compounds may break down on the application of heat into members of other series, resulting in a complex similar to that met with in petroleum. It is most difficult to effect the complete combustion of these compounds discharged at this low temperature and having a high percentage of carbon, without the formation of smoke, the tendency on combustion being to form condensation products in which free carbon predominates, and which is visible, under normal conditions, as smoke.

By low temperature distillation processes the smoke yielding constituents are taken from the coal substance, these constituents being mainly responsible together with the moisture, for the lowering of the temperature under normal conditions.

On combustion of the semi-coke yielded by such treatment, a smokeless condition is maintained by the combustion of the volatile matter in the coke, consisting mainly of methane and hydrogen, together with the combustion of the free carbon in the coke, which under normal domestic conditions, produces the readily combustible carbon monoxide.

Parr and Olin (*loc. cit.*) show the effect of such distillation in graphical manner (Fig. 1).

The portion between A and B represents the constituents of the coal which are driven off at 400° C., and includes the free moisture of the coal (7 per cent.), the water of constitution or combined water of the coal (shown as inert volatile 14 per cent.), and the portion of the true volatile organic matter or combustible volatile, consisting of the heavy hydrocarbons which are responsible for the formation of smoke. From this description of the reactions which take place on heating coal at comparatively low temperatures, it will be seen that low temperature carbonisation cokes possess consequently the property of readily igniting; the coal constituents which are responsible for the depression of the temperature of the heating medium being absent, whilst at the same time they contain, in contrast with gas works or metallurgical cokes, volatile matter which readily ignites. Furthermore the physical nature of the coke is a distinct aid to easy ignition. Cokes obtained at this temperature possess a very open cellular structure, each cell containing air available for combustion and admitting of easy air access.

The fixed carbon in low temperature carbonisation cokes possesses different properties than that formed at higher temperatures, the term fixed carbon being employed in a very wide sense to denote the carbonaceous matter present in coke other than volatile carbonaceous matter. The presence in Carbocoal of a low percentage of volatile organic matter, makes this product more suitable for producer plants, boiler work, furnaces working under forced draught, and anthracite stoves, than for ordinary domestic firegrates.

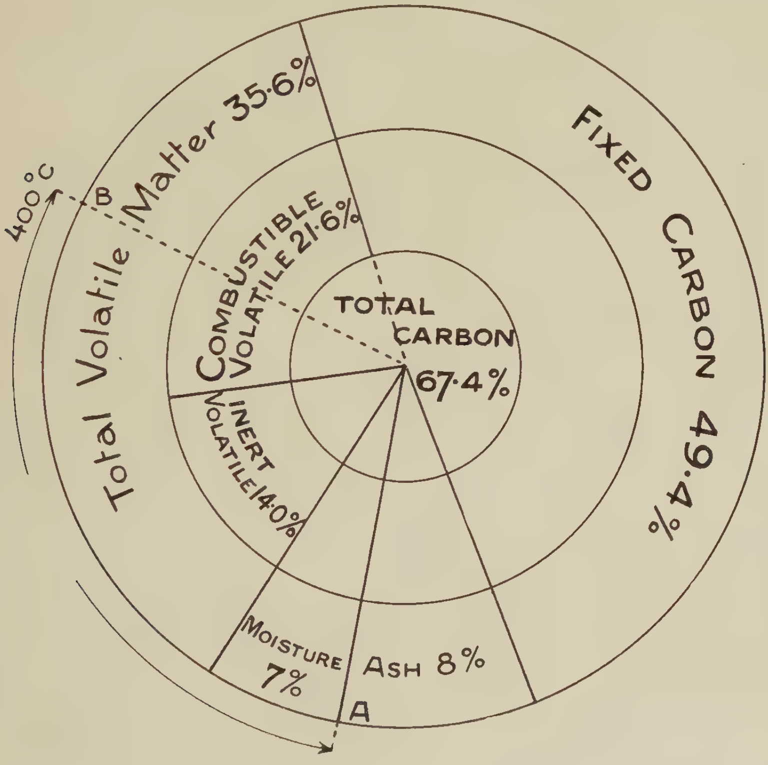


Fig. 1.

On the other hand, the coke produced by the Pure Coal Briquette process is stated to be applicable to any type of plant, it being claimed that by modification in manufacture a coke suitable for domestic purposes, or a coke suitable either for metallurgical work or for general industrial uses can be made.

This claim is based upon the researches which Evans and Sutcliffe have carried out upon the structure of coke. (See Appendix II.) Briefly, they state that ease of ignition is dependent upon the size and distribution of the air cell within the coke mass and upon the nature of the carbon formed in the coke during carbonisation. Those cokes which possess a structure in which the air cells are minute and evenly distributed throughout the mass, and in which the carbon is in a non-graphitic form, will readily ignite and continue to burn.

Whilst such conclusions certainly modify the conception of the influence of the volatile organic matter present in low temperature carbonisation cokes, upon its ease of ignition, it must be clearly understood that the presence in the coke of about 10 per cent. volatile organic matter is a distinct aid to its ease of ignition.

Ash

The ash present in low temperature carbonisation coke is dependent on the inorganic matter present in the coal carbonised, and upon the yield of such coke per unit of coal. The yield of coke under normal conditions is about 75-80 per cent. of the coal carbonised, and the ash in the coke will increase in proportion, *pro rata* with the ash in the coal. It is essential, therefore, that in the manufacture of low temperature carbonisation coke, coal of a reasonable ash content, say below 7 per cent., should be employed, and this is particularly the case where the resulting coke is intended for domestic consumption. Accordingly, it is impossible to produce a satisfactory domestic fuel directly from coals of high ash content, and in any process seeking to work such coals, the tar products must be looked upon as of primary importance. Mention might here be made of the coal washer, which is stated to be an integral part of the present Coalite plant, as by such means a coal of a suitable ash content can be assured, whilst at the same time, serving as a means of mixing non-caking and caking coal to obtain a coal of a definite caking power.

Moisture

The moisture contents of low temperature carbonisation cokes vary considerably, dependent on the nature of the process by which the coke is produced, and on the nature of the coal. In many processes, it is the practice to quench the coke with water immediately on discharge from the retort, and it appears to be only recently that any attempts have been made to conserve the sensible heat of such coke, generating thereby steam which can either be used directly in the process, or utilised in subsequent operations, as for example, in the distillation of the tars produced. Quenching of the coke by water not only causes deterioration in the quality of the coke, from the production of a certain amount of breeze, and the retention by the coke of a large quantity of water, but is also responsible for the production of a coke which crackles and sparks badly on combustion. Maclaurin, in investigating the production of a smokeless fuel by the Maclaurin process, specifically mentions this point as one which caused considerable trouble, and states that the present plant has been modified to overcome the difficulty. In the present Coalite plant, the coke is cooled in air-tight containers, which are water jacketed, the generated steam being utilised in subsidiary operations. The Coalite is allowed to remain in these containers over a charging period (8 hours) and is then sufficiently cool to be easily handled. From analysis of cokes produced in such a way, it is evident that the moisture content is relatively low, and the application of such cooling and heat conservation appears to be one which could be adopted with advantage in many of the methods of high temperature carbonisation at present in vogue.

Heating Value

Cokes prepared by processes in which the coke is not quenched by water, but is obtained as discharged from the retort, are sometimes richer fuels than the original coals from which the cokes were made, the carbonisation having resulted in the removal of certain of the non-combustible contents of the coal substance. Parr and Olin (Bull. No. 60, Eng.Expt.Stat., University of Illinois) give the following table illustrative of this point:—

Samples	B.Th.U's. per lb. as received.	B.Th.U's. after Treatment per lb.	Gain Thermal Units.	Gain Per Cent.	Estimated Loss of Total Noncombustible (Free and Combined Moisture).
Williamson Co.	12,695	13,150	455	3·60	10·30
Saline Co.	13,583	13,746	163	1·63	8·93
Vermilion Co.	12,673	12,892	219	1·72	13·30

Such increase in calorific value depends, however, upon the carbonisation process employed, upon the nature of the coal, and upon the temperature at which carbonisation is carried out, the richest coke being obtained when carbonisation results in the maximum evolution of the non-combustible contents of the coal substance, with a minimum evolution of volatile combustible matter, and a minimum of oxidation.

Uses of Low Temperature Carbonisation Coke

1. *As a Domestic Fuel*

Low temperature carbonisation coke, besides possessing ease of ignition and maintaining a smokeless condition on combustion, also gives out a quantity of radiant heat in excess of that given out by a coal fire of the same dimensions burning under parallel conditions. The heat from a domestic fire is distributed in three ways:—

(*a*) By radiation into the room.
(*b*) By the flow of chimney gases and warm air up the chimney, a portion of this heat passing out into the atmosphere, whilst the remainder heats the chimney stack and adjacent brickwork above the fire, and
(*c*) Heat imparted to the immediate surroundings and conducted by them into the walls of the room.

The heat radiated into a room from a domestic fire, and in a minor degree the heat lost in the air current passing up the chimney, but employed in constantly drawing air into the room, ensuring ventilation, are the most important. Consequently the radiant heat of a domestic fire may be taken as a direct indication of its efficiency. At the instigation of the Manchester Corporation Air Pollution Advisory Board, Dr. Fishenden has carried out measurements of such radiant heat ("The Coal Fire," Margaret White Fishenden, D.Sc., Fuel Research Board, Special Report No. 3), and besides comparing grates of different construction, has compared the radiant efficiency of various types of fuels. The radiant efficiency was taken as the percentage of the total energy of combustion of the fuel consumed, which entered the room as radiant heat. The following table shows the results obtained by Dr. Fishenden :—

Type of Fuel	*Radiant Efficiency*	*Remarks*
(1) High Class House Coal (13,900-14,500 B.Th.U's. per lb.) .	19·5-24%	
(2) Above Coal as Slack	20%	This value corresponds with 24% on No. 1, i.e., a reduction in radiant efficiency.
(3) Welsh Anthracite (14,400 B.Th.U's. per lb.)	27% in a grate giving 24% with coal fires.	
(4) Dry Gas Coke (13,000 B.Th.U's. per lb.)	24·5-28·5% compared with 21·0-24·0% with coal fires under parallel conditions.	If the moisture content of the coke increased, the radiant efficiency decreased, the diminution in the aggregate quantity of radiation being more than the equivalent amount of heat required to vaporise the water present. For contents of more than say 10% the radiation was less than for an equal weight of coal.
(5) Low Temperature Carbonisation Cokes (13,200 B.Th.U's. per lb.)	Dry Cokes 31-34%	As in the above case, the moisture content affected the radiant efficiency, but with the coke containing the highest percentage of water (11%), the aggregate radiation was considerably in excess of that given out by an equal weight of coal.
(6) Briquettes (11,200 B.Th.U's. Moisture 7½%)	19% compared with 24% for coal under parallel conditions.	

In a further research (The Efficiency of Low Temperature Coke in Domestic Appliances, Margaret White Fishenden, D.Sc.—Technical Paper No. 3—Fuel Research Board), Dr.

Fishenden investigated the efficiency of several low temperature carbonisation cokes in various types of kitchen ranges and sitting-room grates. The conclusions reached are as follows :—

" *Bituminous Coal versus Low Temperature Carbonisation Coke Cakes for Domestic Use*

" In most of the appliances tested, low temperature carbonisation coke cakes yielded a greater proportion of their total heat of combustion either for radiation or for water heating than bituminous coal. Further, as the following figures clearly demonstrate, the higher the efficiency of the apparatus, the greater was the relative advantage of the coke cakes over coal, whether for radiation or water heating. The exact value of the latter depends, of course, upon the temperature attained, and also upon the size, position, and insulation of the pipes and cylinder, and the time the water stands in the cylinder. The results refer to experiments carried out under practical conditions, the water having generally been run off as it reached temperatures about suitable for domestic purposes.

Radiation—Mean Efficiency.

Grate.	Coal.	Coke Cakes.	Percentage Difference.
"D"	24·2	30·8	27
"A"	19.5	24·0	23
"E"	17·3	19·9	15

Water Heating—Mean Efficiency.

Grate.	Coal.	Coke Cakes.	Percentage Difference.
"G"	32·0	42·0	32
"F"	17·3	20·7	20
"H"	15·2	17·4	14
"J"	13·1	14·5	11

" In the case of ranges H and J, the differences are slightly exaggerated, as the temperatures reached by the water were some 10 degrees higher for coal than for coke cake fires.

" The comparative behaviour of the two fuels, weight for weight, will obviously be dependent upon the relative calorific values, but it is apparent that the calorific value of a bituminous coal must, in all cases, be considerably above that of the low temperature carbonisation fuel, if it is to give equal weight for weight results.

" For oven heating, the coke cakes compared rather less favourably with coal, and roughly about equal numbers of heat units were needed to give similar results. The advantage of the coke cakes, in fact, appears to be largely due to radiation effects, and is most marked when the distance between the fuel bed and the oven or boiler to be heated is low.

" Where the distance between the fuel bed and the oven or boiler is great, the superiority of the coke cakes is diminished, or even in certain cases may disappear, the flame contact from the bituminous coal apparently more than counterbalancing the higher radiation from the coke cakes. It must, however, be borne in mind that such comparisons refer to ovens and boilers planned to burn coal, and there is little doubt that in appliances specially designed for the burning of low temperature carbonisation fuels, the superiority of the latter might be considerably emphasised."

2. *As a Producer Fuel*

In so far as the bulk of the tar-producing bodies are removed from a bituminous coal by low temperature carbonisation, the coke produced appears to be eminently suitable for use in producers. In the Maclaurin process, provision is made for total gasification of the coke, with the recovery of the low temperature tar products, air and steam being blown into the second chamber A (Fig. 10, p. 104) by passage E, indicated by dotted lines, the gas, in ascending, carbonising the fuel and distilling off the oils, which are recovered in the usual way.

Maclaurin states (J.Soc.Chem.Ind., 1917, 36, 620) that " A fairly uniform power gas is therefore easily maintained, and as there is no destruction of the oils, the gas is perfectly free from . . . masses of tar." The length of the producer enables the carbon in the fuel to be burned practically completely. With the coals tried, clinkering difficulties hardly appeared, although the steam used was occasionally very low. The following is a typical analysis of the power gas made :—CO_2 12·9 per cent., O_2 0·9 per cent., C_nH_{2n} 0·2 per cent., CO 5·6 per cent., CH_4 10·0 per cent., H_2 8·9 per cent., N_2 61·5 per cent. Calculated heating value = 134 B.Th.U's. per c. ft.

Parr and Olin (Bulletin No. 70, Eng.Expt.Stat., University of Illinois) give the results of a producer test carried out on a low temperature carbonisation coke, made from Vermilion County coal, an " Otto " suction producer designed for anthracite being employed. They conclude that " the producer ran successfully and gave little trouble." Owing to the tendency of the fuel to coke and arch, and to its lightness, it was found necessary to poke the fuel bed more often than when anthracite was employed, but on the other hand, there was a remarkable freedom from ash and clinkering difficulties, small pieces of clinker being found in the ash but no clinker sticking to the sides of the producer where it usually accumulates. Samples of gas, taken from the gas main leaving the producer, showed that the quantity of tar in the gas was negligible.

The efficiencies obtained, using this fuel, were respectively 74·4 per cent. for hot gas and 64·9 per cent. for cold gas, comparing very favourably with anthracite.

The following tables show the composition and consumption of the producer fuel, and gives details of the make, efficiency, and composition of the gas :—

Composition of Producer Fuel

Fixed carbon per cent.	70·70
Volatile matter per cent	18·00
Moisture per cent.	2·28
Ash per cent.	15·82
Sulphur (separately determined) per cent.	3·13

Ultimate Composition of Producer Fuel

Carbon per cent.	71·50
Hydrogen per cent.	2·82
Oxygen per cent.	5·26
Nitrogen per cent.	1·02
Sulphur per cent.	3·20
Ash per cent.	16·20
Moisture in sample as received, per cent.	2·28
Calorific Value, per lb., dry coal, B.Th.U's.	11,601

Fuel Consumption per hour

Dry coal per hour, lb.	58·8
Dry coal per sq. ft. of grate area per hour, lb.	35·3
Dry coal per sq ft. of fuel bed per hour, lb.	31·3

Gas

Calorific value per c. ft. of standard gas from calorimeter. (High Value) B.Th.U's	121
Specific weight of standard gas, lb., per c. ft.	0·0670
Specific heat of dry gas leaving producer (estimated)	0·260
Total volume of gas from meters, c. ft.	26,927
Total Volume of standard gas (at 16·5° C. and 30 in.) c. ft.	23,150
Volume of standard gas per hour c. ft.	3,660
Volume of standard gas per lb. of dry coal c. ft.	62·3
Total weight of standard gas, lb.	1,552
Weight of standard gas per lb. of dry coal, lb.	4·17

Percentage Composition of Gas	By Volume	By Weight
CO_3	4·15	7·19
CO	21·10	23·17
O_2	0·30	0·38
H_2 (estimated from calorific value)	11·80	0·93
CH_4	1·50	0·96
N_2 by difference	61·00	67·37

Efficiency

Grate Efficiency, per cent	92·2
Hot gas efficiency, based on high heating value per cent.	74·4
Cold gas efficiency, based on low heating value per cent.	64·9

NOTE.—Coal here refers to low temperature carbonisation coke from Vermilion County coal.

3. For Steam-Raising and General Industrial Purposes

The quantity of low temperature carbonisation coke hitherto manufactured has not admitted of its use for general industrial purposes, and the main object has been to supply a smokeless domestic fuel. At the same time, should the problems incidental to the low temperature carbonisation of coal be solved on plant, economically and commercially sound, producing in bulk, it is possible that semi-coke may be used to the entire exclusion of raw coal. No tests are available to show its efficiency in, say, ordinary steam-raising plant, such as Lancashire boilers. Since a large proportion of its thermal energy is given out as radiant heat and as there would be practically no flame contact with the surfaces to be heated, modifications of existing plant may be necessary to ensure maximum efficiency.

On the other hand, the advances foreshadowed in the applications of pulverised fuel and producer gas to industrial plant may indicate the lines upon which low temperature carbonisation coke may be used, particularly as it is comparatively easy to make from a non-caking coal, a finely divided friable semi-coke eminently suitable for pulverisation and use in this form, such as is produced in the L.M.N. and other types of rotary retorts, and in the primary carbonisation of the Carbocoal process.

It has been claimed by the inventors of several processes that it is possible to manufacture a metallurgical coke by the low temperature carbonisation of coal. At the present time, no satisfactory figures are available to indicate the price per ton of such coke compared with the price per ton of metallurgical coke produced in normal by-product coke-oven practice. Furthermore, the claims made with regard to the suitability of this coke for metallurgical work have not been entirely substantiated. On the other hand, the coke produced by modifications of the Pure Coal Briquette process appears to possess many obvious advantages which are dealt with in the description of this process.

CHAPTER V

PROCESSES

INTRODUCTORY—TYPES OF RETORT—ADVANTAGES AND DISADVANTAGES OF EACH TYPE—PRE-TREATMENT OF COAL—THE ECONOMICS OF LOW TEMPERATURE CARBONISATION—TYPICAL PROCESSES—COALITE—CARBOCOAL—MACLAURIN—L.M.N.—PURE COAL BRIQUETTE—DEL MONTE—TOZER—CHISWICK—FISCHER AND GLUUD—FUEL RESEARCH STATION EXPERIMENTAL RETORT—SUMMERS—FREEMAN—TRAER—FUSION — GREEN-LAUCKS — TURNER — WALLACE — RAFFLOER — THYSSEN—THOMAS—THIERY—ILLINGWORTH.

Recently, the solution of the problems attendant on the carbonisation of coal at low temperatures has been likened in importance, in relation to the industry of this country, to the invention of the steam engine, and it has been prophesied that the solution will be the commencement of another era of industrial prosperity and progress, equal to, if not exceeding, the progress which has been witnessed since the days of Watt. The discovery which matured in the mind of Watt, as he made his classical researches on the kettle of boiling water, may find a parallel in the ideals which moved Scott Moncrieff and Parker. What subsequent investigators have failed to realise is that the birth of any great invention is a process full of painstaking care and labour, and only finding comparative completion after many years. They have, rather, been optimistic beyond the bounds of reason, and have failed in so far that they have not understood the essentials upon which such a solution rests.

S. Roy Illingworth, in a recent paper before the South Wales Institute of Engineers, said: " Different people have proposed many and varied mechanical means for the treatment of coal at low temperatures, due to the fact that man knows little about the constitution of coal, yet hopes that by either sheer brutality, cajolery, or flattery, coal will amend to his designs. The solution of the problem rests in the first place with the chemist; its successful exploitation is in the hands of the chemical engineer and the business man who realises what the initial productive operations entail. The chemical constitution of coal is the first plank, the keystone of the problem, associated with which is the problem of the pyrogenetic chemistry of hydrocarbons."

On the other hand, much ingenuity has been exercised by numerous investigators, and during the past few years valuable information and knowledge have been gained. The Fuel Research Board in its report for the years 1920, 1921 (Second Section: Low Temperature Carbonisation, H.M. Stationery Office), viewing the situation at the present time, gives a conditional "Yes" to the question—"Will it be possible to establish on sound industrial lines a new industry based on the carbonisation of the tens of millions of tons of coal per annum, which are at present being consumed in the raw state?" . . . "the elements of uncertainty being mainly economic and social."

Processes representative of the lines upon which the solution of the problem has been attempted are given in detail in this chapter. Processes may be roughly divided into three classes, according to the type of retort employed, namely:—

(1) Externally heated retorts in which the coal is exposed in very thin layers (about four inches) to heat supplied from an external combustion chamber, by radiation, conduction and convection, and in which the coal is stationary in the retort during carbonisation. The present Coalite process furnishes an example of this type of retort.

(2) Externally heated retorts in which the coal is mechanically propelled through the retort and continually stirred during carbonisation to expose fresh surfaces and subjected to heat radiated, conducted and convected from an external combustion chamber. Such a retort is employed in the primary carbonisation of the Carbocoal process.

(3) Retorts to which internal heat is applied, carbonisation being effected by means of a stream of hot producer gas or coal gas, passing directly through the mass of the coal in the retort. The Maclaurin, the L.M.N., and the Pure

Coal Briquette processes utilise retorts built upon this principle.

In any system of carbonisation, the throughput per retort per day is a vital economic consideration, directly affected by the conductivity of the coal mass within the retort, at any particular temperature. The classes of retort enumerated above represent the three methods which have been adopted for overcoming the low heat transmission of a mass of coal at low temperatures, namely, heating the coal in thin layers, agitating the mass of coal to expose fresh surfaces to the hot walls of the retort, and heating the coal by means of a hot stream of gas which comes into intimate contact with each individual particle of coal.

Retorts belonging to the first class suffer from their low capacity or from the large surface area of retort wall which must be maintained at a uniform temperature. Those of the second class are at a disadvantage in so far as the low temperature carbonisation coke obtained is in a broken condition, necessitating further treatment such as briquetting if the product is to be available for domestic purposes, and within limits for industrial purposes. Retorts in the third class have so far necessitated the use of large volumes of gas of low calorific value for which an outlet must be found, and are limited in application. Otherwise, any system in which carbonisation is carried out by a hot stream of gas, appear to be the most satisfactory, for by this means not only is the difficulty of poor heat transmission of the coal overcome, but to a certain extent the difficulty encountered due to swelling of the coal charge is obviated. Several inventors have advocated the use of superheated steam, and the retort designed by C. Turner, and at present in experimental operation on the Norfolk shale deposits, is certainly worthy of mention in this connection. The retort used in the Pure Coal Briquette process is constructed upon similar lines to that of the Del Monte retort in so far as the gas evolved from a previous charge, after purification, is re-heated, and used in the carbonisation of a succeeding charge. No large units of the Pure Coal Briquette process have yet, however, been erected, and the remarkable claims of this process have still to be substantiated on an industrial scale, although the inventors claim that small scale plant has been operated successfully for a considerable number of years. The pyrogenetic chemistry of the hydrocarbons bears largely upon this point, and as S. Roy Illingworth says, this is of primary importance in the solution of the main problem.

In certain processes, the coal receives either pre-treatment other than the preliminary washing of the coal to a reasonable ash content, or treatment after carbonisation to obtain a semi-coke in a marketable form, whereas other processes are parallel to the ordinary gas works process in so far as the clean coal is carbonised directly and marketed as obtained from the retort.

One of the commonest methods of pre-treatment, which has only come into operation within comparatively recent years, consists in blending or mixing the coal either with a coke obtained from a previous charge, or mixing together a non-coking and a coking coal in order to obtain a product which will not swell excessively on carbonisation and cause " sticking up " of the coal in the retort. Such blending is often carried out in washing plant so that blending and cleaning become one operation. The mixing must be carried out in the correct proportions of the component coals, and consequently the feeding of the materials to the washer must be carefully regulated. In the present Coalite plant at Barnsley the coal is fed by hand into the " Notanos " washer, but in larger scale plant the feed would have to be mechanically controlled.

The Pure Coal Briquette process presents a unique case in the treatment of coal prior to carbonisation, the pulverisation, blending, and briquetting of the coal being the essential feature of the process. The blending of coal places a limit upon the size of coal which can be efficiently used in a process in which blending is essential, it being increasingly difficult to obtain an intimate mixture for carbonisation and a uniform coke product, as the coal increases in size. In the above process, blending is carried out along with pulverisation, and in consequence a very intimate mixture is obtained, resulting in a uniform product.

Treatment subsequent to carbonisation consists in the briquetting of the coke obtained, and in some cases, the carbonisation of the briquettes at a high temperature as in the Carbocoal process.

The L.M.N. and Maclaurin processes present cases in which the coal receives no special treatment either before or after carbonisation.

The first five processes, given in detail in this chapter, represent processes characteristic of the methods employed in overcoming technical difficulties.

In the consideration of any low temperature carbonisation process two aspects are presented:

(1) Are the difficulties attendant on the low temperature carbonisation of the coal satisfactorily overcome?
(2) What value do the products command in relation to the cost of the process? or put more tersely—does it pay?

These aspects are inter-related.

Judged purely from the point of view of production, as distinct from economic considerations, satisfactory smokeless fuel in small quantities has been produced by several processes, and in so far the problem has been solved. On the other hand, this partial solution has resulted in other problems arising, consisting mainly in the utilisation of the by-products obtained—namely, the tar and gas.

The gas industry as a whole has been inclined, up to the present time, to regard those interested in low temperature carbonisation with disfavour, if not actually exhibiting open antagonism, fearing perhaps that the safety of the gas industry was endangered with the rise of this new conception of carbonisation. It must, however, be realised that a union will eventually take place between the old and the new industries, in having one common interest, namely, the gas produced by the two methods of carbonisation.

Whilst carbonisation at low temperatures can never replace carbonisation at high temperatures for the production of gas, the new processes will provide a gas which will serve as an enriching agent for the gas now produced by steaming in gas-works retorts.

In future, gas undertakings are to supply consumers on a basis of cost per therm, instead of on the basis of cost per cubic foot of gas supplied. The fixing of a suitable calorific value for the gas for sale under the new regulations has to be considered from the point of view of the cost of carbonisation per cubic foot of gas, and the cost of distribution per therm supplied to the consumer.

Reduction in the cost of carbonisation per cubic foot of gas produced entails the conversion of a maximum amount of coke to saleable gas by steaming, and consequently the production of a gas of lower calorific value. At the same time, with existing distributing systems, a limit is placed upon this calorific value from a consideration of the therms supplied to the consumer, and the capacity of the system. Consequently, between production and distribution there exists, therefore, what might be termed an economic calorific value for the gas, and this has been determined to lie, with large undertakings, in the region of 450-500 B.Th.U's. per c. ft. To obtain a gas of this calorific value, enrichment by means of carburetted water gas is resorted to, a comparatively costly operation entailing the use of large quantities of this gas.

Certain low temperature carbonisation processes, such as the Coalite process, produce gas of a very high calorific value, much in excess of that of carburetted water gas. At the present time, it is being utilised to enrich producer gas for the heating of the retorts used in these processes, but it will probably furnish the link between the two industries, possessing so obvious an application in the gas industry.

With regard to what is perhaps the chief by-product of all low temperature carbonisation processes—the tar—problems arising from its utilisation appear to have been lost sight of in regarding such tar solely as fuel oil.

Owing to the fact that the supplies of fuel oil of all kinds for home consumption are dependent on overseas sources, the low temperature carbonisation of coal as a possible home source is rightly regarded as of national importance. That the Government is alive to its importance is evident from a perusal of official publications which have appeared within recent years (e.g., Report of the Fuel Research Board for the years 1918-1919 (pp. 6-10) and for the years 1920-1921). In consequence, perhaps, the tendency has been to regard low temperature tar purely as fuel oil, and its possibilities in other directions have been overlooked. Much investigation has yet to be made on the nature of low temperature tar, and it is possible that on such investigation the ultimate commercial issue of low temperature carbonisation processes may rest.

The coal tar produced by the gas works process has been transformed from what was practically a waste product to one which is now the basis of many industries, and which has become virtually a necessity to our everyday life. We may find that the utilisation of low temperature tar as fuel oil in normal times will come to be regarded as an uneconomical proceeding.

Low temperature carbonisation processes have been placed before the public in prospectuses in which the products are largely hypothetical, calculations being based upon the results obtained on small scale plant.

It is often stated that a process will produce so many cwt. of smokeless fuel, so many gallons of motor spirit, lubricating oils of various grades, a tar from which valuable dyes can be manufactured and high yields of ammonium sulphate, per ton of coal carbonised. As already stated, smokeless fuel can be readily produced, and under certain conditions high yields of ammonium sulphate can be obtained, but the remainder of the products which appear so attractive in a prospectus are never attained in actual working, being dependent upon the nature of material carbonised, and upon the system of carbonisation employed.

This naturally leads to the second consideration of any low temperature carbonisation process, namely, what value do the products command in relation to the cost of the process? Judged from the standpoint of the national well-being, and placing to the credit side of any process the enormous saving which would be effected by the abolition of black smoke in the health of the community, and in the benefit to structures and vegetation, together with the establishment of a home supply of fuel oil, and the conservation of our coal reserves, many low temperature carbonisation processes at present extant might be regarded as paying propositions. But under present conditions when a process must stand or fall according to the dividends declared, the question " Does it pay " is more difficult to answer.

It is, perhaps, best approached by considering the value of each individual product, at the present time, and the factors which may influence this value in the future.

The most important product is the coke, since each ton of coal carbonised yields approximately 15 cwt. of coke. Such coke as is produced by low temperature carbonisation processes has been offered in the open market at a price delivered to the consumer in excess of that at which best household coal is sold. Low temperature coke generally occupies a greater space than that occupied by an equal weight of coal, a fact which materially affects the cost of transport from the producer to the consumer, and modifies any advantage which the consumer might have in a reduced consumption, due to the increased bulk. Under these circumstances, this coke finds a sale only to those interested in some measure in its production, or in the Smoke Abatement question. Before the demand for low temperature coke can become insistent, either its cost must be equal to, or lower than that of coal, or the public must be educated to its advantages and be willing to pay for them; the prohibition by legislation of the burning of raw coal is an alternative.

For any process to pay at the present time on a large industrial scale, it must produce the coke at a price comparable with the price obtaining for coal for a like purpose.

Special consideration is demanded by those processes in which the coal is blended with coke, prior to carbonisation, to prevent swelling of the charge. Such coke will yield practically no by-products on subsequent carbonisation, and the throughput of the retort will be reduced accordingly. Consequently a non-caking coal is preferable to coke, as an agent for modifying the swelling properties of a coal.

The gas produced by low temperature carbonisation processes varies in quality and quantity according to the type of process employed. The processes producing large volumes of low grade gas demand special consideration, in so far as these must depend for their successful operation upon their linking up with other industries in which large volumes of such gas can be employed. The L.M.N. process has been specially designed for co-operation with the steel industry, and here, the economics of the process must be considered in conjunction with the economics of producer gas manufacture for steel production. Similarly with other processes of a like nature, as for example that of Maclaurin, the success of the process lies largely in the method of utilisation of the gas.

The outlet for the rich hydrocarbon gas produced by those processes in which the coal is carbonised in externally heated retorts, is at present mainly in the enrichment of producer gas manufactured to heat such retorts. Reference has already been made to its future outlet as an enriching agent for gas of low calorific value produced by steaming in gas retorts. In order then to write down this gas at its fullest value, the close co-operation of the gas industry, or a similar outlet, must be secured by any low temperature carbonisation process.

Speaking of the utilisation of the gas in this manner, the Fuel Research Board* state that " The potential value of the gas obtained from one ton of coal carbonised at 600° C. may be taken as 30 therms, which, at the very moderate price of fourpence per therm, would realise ten shillings per ton of coal carbonised. As the value of the gas for enriching purposes becomes generally realised, this product will take its place as one of the most valuable, and at the same time the least speculative of the assets of low temperature carbonisation." Otherwise, by utilisation in the process itself, its value is considerably reduced, and can only be approximated.

The yield of ammonium sulphate per ton of coal carbonised varies with the several low temperature carbonisation processes described later, and the value of this product will vary with the demand existing at any one time.

The remaining by-product of the low temperature carbonisation of coal, the tar or oil, presents, perhaps, the most difficult problem of all.

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* Report of the Fuel Research Board for the years 1920, 1921. Second Section: Low Temperature Carbonisation.

Lander (representing the Fuel Research Board) in a recent paper before the South Wales Institute of Engineers, discussing the utilisation of low temperature tar or oil, as fuel oil, said: "During the past eighteen months the price of fuel oil has fallen from over £15 per ton to from £3 to £4. The bearing of this fall in price upon schemes for the low temperature carbonisation of coal will at once be appreciated when it is stated that this represents a drop of at least ten shillings on the value of the fuel oil obtainable by carbonisation from one ton of coal."

This statement serves to emphasise the need to which reference has already been made for a concentration of research work upon the constitution of such tar or oil. At the present time, its value can be written down as fourpence per gallon, a price which may vary with conditions entirely outside the control of those financially interested in any low temperature carbonisation process, and which may mean the success or failure of the process. On the other hand, research work may give an entirely different aspect to the value of the tar or oils.

The question as to whether any low temperature carbonisation process will pay, may, therefore, be summed up somewhat in the following manner, provided that the yields of coke, gas, tar, and ammonium sulphate supplied by the various advocates of the process can be relied upon.

Per Ton of Coal Carbonised.

Debit.

1. Capital Outlay and Depreciation.	Can be estimated fairly correctly.
2. Maintenance of Plant and Overhead Charges	
3. Labour and Supervision.	
4. Power, etc.	
5. Cost of Coal Carbonised.	Dependent on market conditions, and affecting equally all carbonising systems, whether high or low temperature,

Credit.

1. Coke—approximately 15 cwt.—finding a value comparable with that of coal of a similar quality.
2. Ammonium sulphate—varying yield—finding the market value.
3. Gas—3,000-6,000 c. ft. of gas of high calorific value—finding at present, utilisation in the process—in the future, a value dependent on the value of the gas per therm to an established gas undertaking.
4. Tar and oils—approximately 20 gallons—finding at present, the current value of fuel oil—in the future, a value dependent on the fuller knowledge of its constitution, and the possibility of subsequent working up into more valuable products.

From all other processes for the production of smokeless fuel, the comparatively recent Pure Coal Briquette process stands out as unique in its application, and criticism of this process is perhaps best reserved until its possibilities have been tried out on large scale plant.

The Coalite Process

The Coalite process has undergone considerable modification since its inception immediately following Parker's original patents (Patents Nos. 14,365 and 17,347, 1906) and at the present time the process appears to promise some fair measure of success.

The modern process, herein described, is at present being worked by Messrs. Low Temperature Carbonisation Limited, Barugh, Barnsley, Yorkshire, who are the successors of Coalite Limited and of the concerns operating Parker's numerous patents. The following description does not seek to establish the economic aspects of the process, as up to the present, the process has not been worked for a sufficient period to warrant any expression being made of its commercial success. The principles upon which the present process is based, are, however, fundamentally sound—for example, the utilisation of a coal of low ash content, which possesses at the same time a known caking property, the evacuation of the evolved gases and tar into a cool receptacle, thus minimising decomposition of the volatile matter, and the employment of mechanism, which, it is claimed overcomes the paramount difficulty due to the swelling of coals during low temperature carbonisation.

The process is purely and simply a low temperature distillation process, in which special plant is employed to overcome the difficulties encountered in low temperature carbonisation, distillation taking place at a temperature of about 550° C., dependent on the type of coal carbonised. The temperature of carbonisation employed to ensure maximum yields is determined experimentally, prior to a complete carbonisation being made, this test carbonisation being carried out in large scale laboratory plant.

Outline of Process

The coals to be carbonised (a mixture of 30 per cent. coking slack (Parkgate) and 70 per cent. non-coking slack (Claycross) is at present employed) are fed into a coal washer, the particular type at present in use being a " Notanos " coal washer. Here the mixing takes place, and at the same time, the ash in the respective slacks is reduced to a working figure of about 4-6 per cent. From this washer the coal mixture is passed by means of belt and bucket conveyors to draining bunkers, and subsequently to storage bunkers to await use. From the latter the coal is passed by a conveyor to charging hoppers situated over each individual retort. These hoppers can be clearly seen in Fig. 2 showing the gallery of the charging hoppers for a full setting

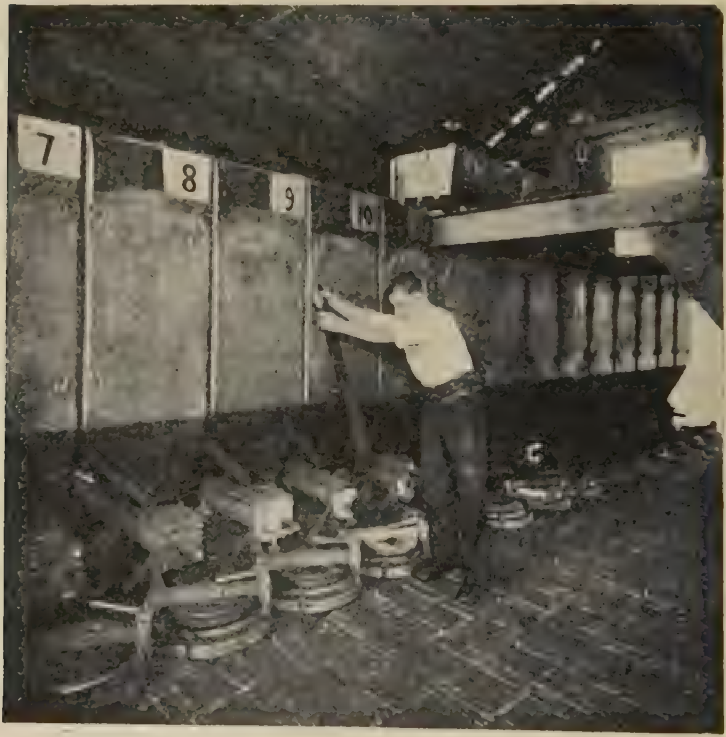

Fig. 2.—Coalite Process
Gallery of Charging Hoppers

of retorts, and are made of such a size as to hold coal sufficient for the charging of one retort. Each charging hopper is provided with a rotary valve, which is operated by a hand lever, by means of which the charge is admitted to the retort. Each retort is an individual unit and can be operated separately. The retorts demand particular notice, as it is claimed that, owing to their special construction, the swelling and sticking difficulties encountered in carbonising

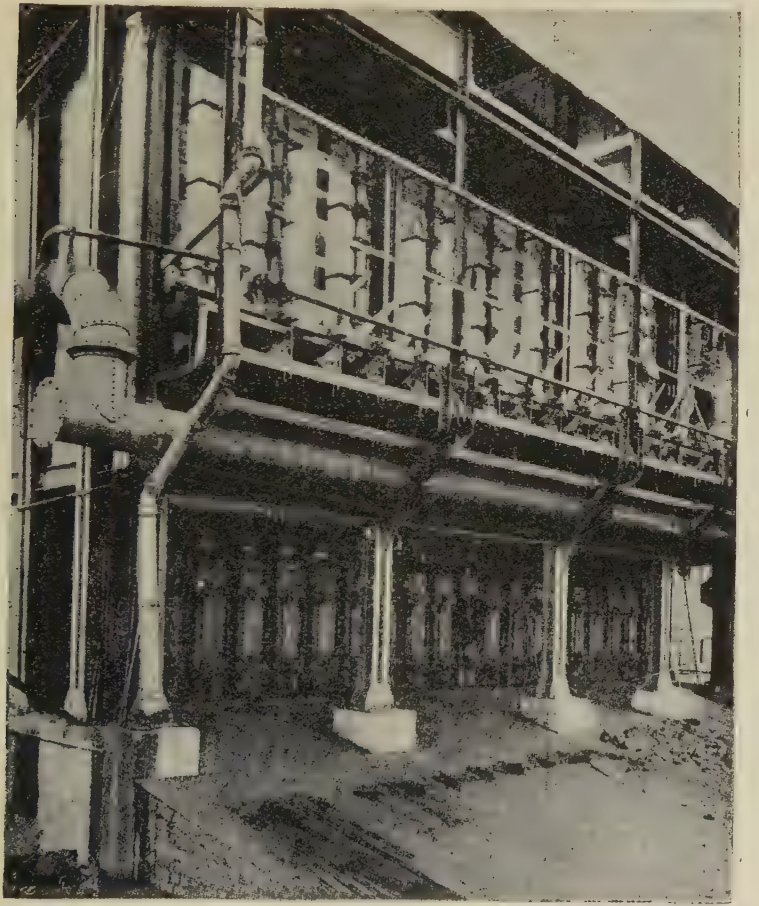

FIG. 3.—COALITE PROCESS
VIEW OF RETORTS

coal at low temperatures have been overcome. The construction of the retorts is shown in Figs. 3 and 4. The retorts are built of fire brick, each retort being 9 ft. 6 ins. in depth, 7 ft. 3 ins. to 7 ft. 6 ins. in length, tapering from top to bottom and having an average width of 11 ins.

The distance from centre to centre of the retorts is 21 ins. The outstanding feature of these retorts lies in the provision of two plates situated inside and running the whole depth of the retort, the plates being made of manganese cast iron, to withstand rough usage, without suffering undue growth or warping. The plates are carried on a bridge spindle situated on a bridge piece. This spindle, which can be partially rotated by means of a ratchet lever and ratchet wheel, is operated from the top of the retort, and is inserted in a small manhole fixed just below the operating gear of the charging hoppers. The bridge spindle is carried in cast-iron bearings, which are so made that, if necessary, the whole of this internal apparatus in the retort can be withdrawn at the top. The retort plates are perforated, so that the gas and tar evolved during the carbonisation of the charge pass out through the perforations into the free space between the plates, which is comparatively cool, and consequently cracking or decomposition of these evolved matters is minimised. In other types of retort in which the gases have to find outlet through a heated mass of coal, such cracking is considerable.

The plates are 9 ft. 6 ins. by 6 ft. 5 ins., and are in three sections for convenience of manufacture, being afterwards bolted together. They are provided with small flanges at intervals to prevent the charged coal from compressing them. The bridge piece, supporting the bridge-spindle, is so placed that when the two plates in the retort are level with one another, it prevents the stream of coal from the charging hopper passing in between the plates, directing it into the space between the outside of the plates and the inside of the retort walls.

The flanges, situated at the extreme ends of the plates, are connected together with a small link which, whilst admitting movement of the plates, hold them at a predetermined distance apart. By means of the ratchet lever and ratchet

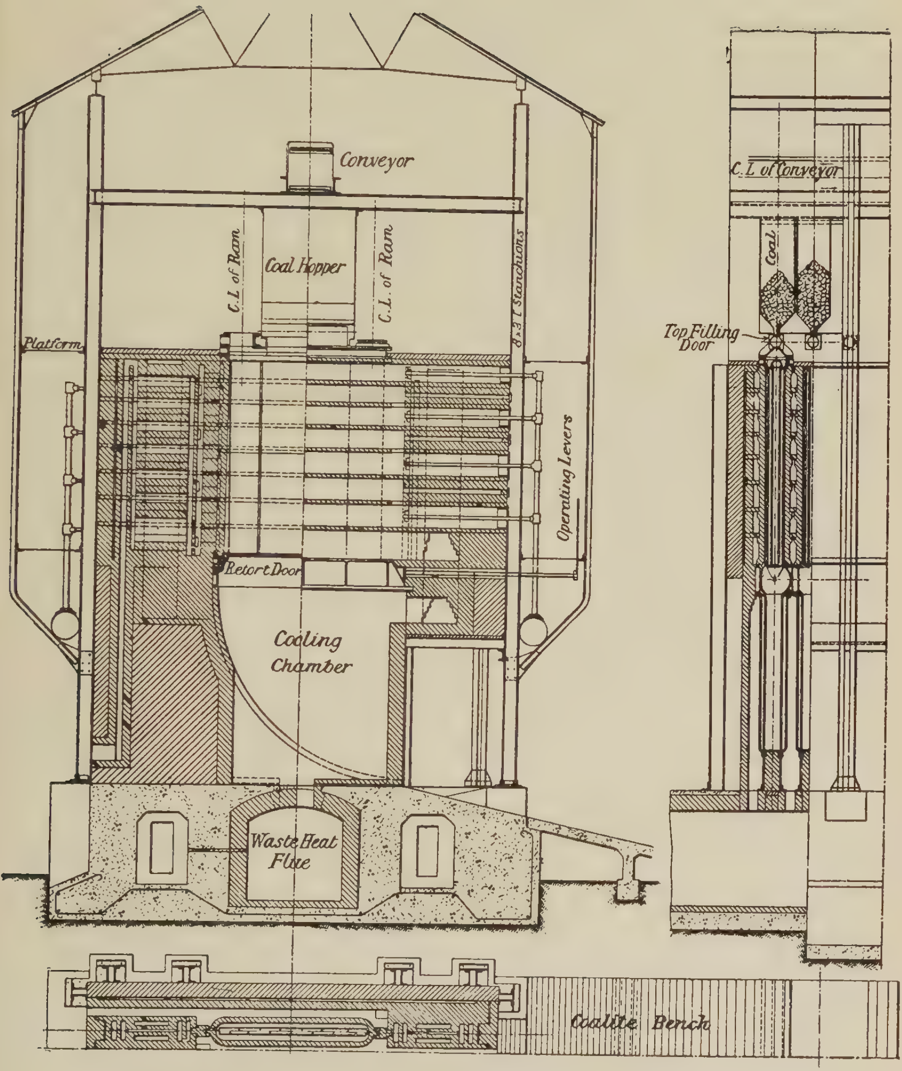

FIG. 4.—COALITE PROCESS
SECTIONAL ELEVATION THROUGH THE RETORTS

wheel these plates can be moved in opposite directions, causing the flanges to disengage, and the plates are brought closer together so that the carbonised charge is now free to fall into a receptacle below the retort. The arrangement and movement of the plates are shown in Fig. 5. The retort rests upon a cast-iron casing containing a rocking cylinder valve, upon which the charge rests prior to carbonisation. This valve is operated by a lever, which is placed outside the retort, and is available from a working gallery running the whole length of the setting, and situated above the discharge chambers.

As the retorts are built in close proximity to one another, successive rocking cylinder valve levers are grouped in series of four. Arrangements are made whereby steam can be generated by the heat of the hot charge, so that it is possible to steam the charge, with the object of increasing the yield of ammonia. When the carbonisation of a charge is completed, the plates are brought nearer together, the rocking cylinder valve is opened, and the charge falls into the cooling chamber below. A poking hole is provided above the retort just below the entrance from the charging hopper for use in case the charge still sticks in the retort. The cooling chamber is constructed of sheet steel, and is surrounded with water, being provided with baffles so that a constant circulation of water is provided, and the sensible heat of the coalite from the retort is thus absorbed, the temperature being sufficiently reduced to enable the material to be handled immediately it leaves the cooling chamber. The coalite is thus obtained quite dry in a hard cake, its value being unimpaired either by direct water cooling or by combustion, whilst the sensible heat from it is conserved. Cooling of a charge can be accomplished in two hours, but as complete carbonisation of a charge requires eight hours, the coalite is left in the cooling chamber throughout this period, i.e., until the succeeding charge is ready for discharging. The steam generated in the cooling chamber can be subsequently used for tar distillation or for other purposes.

When the charge is cooled, the door of the cooling chamber is opened, and the coalite raked out, the raking being facilitated by the sloping back of the chamber. The door of the cooling chamber is set with asbestos packing, forming a perfectly gas-tight joint, and is provided with a patent locking device.

The retorts are heated either by gas from the carbonised charge, freed from tar, light spirit, and ammonia, or by gas otherwise generated. The high calorific value of the gas generated within the retort is counterbalanced by its low yield, and the present plant has not progressed sufficiently yet to determine definitely if the generated gas will be sufficient to completely heat the retorts without being supplemented from an outside source.

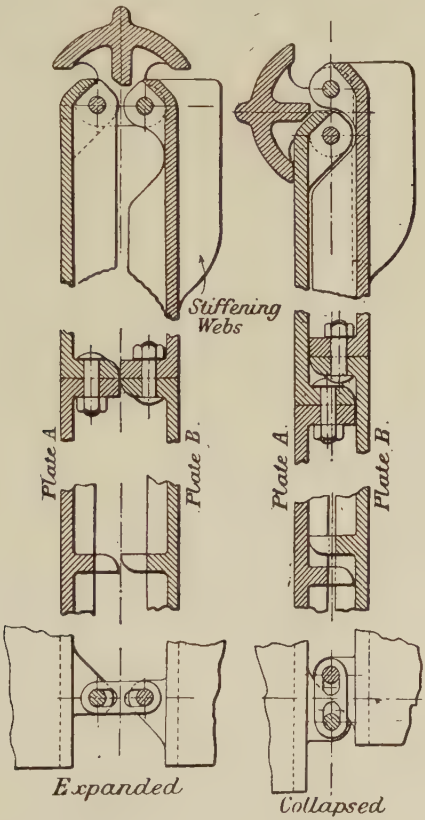

Fig. 5.—Coalite Process
Retort Plates

At the present time, the gas generated through the carbonisation is being supplemented by a supply of Mond producer gas.

The mixed gas is supplied to the retorts through two large gas mains running horizontally along both sides of the setting, and from these mains is conducted through vertical and horizontal pipes to the setting. No special burners are used, the gas being simply ignited as it issues from the horizontal pipes. By the arrangement of the setting, the hot gases of combustion are led downwards, past successive burners, the direction being controlled by dampers, and the waste gases from the whole of the burners finally pass out into regenerative settings. These arrangements are shown in Fig 6.

The evolved tar and gas is taken off into a foul main, and the tar extraction, scrubbing and sulphate plant, and storage arrangements are similar to those employed in ordinary gas works practice.

The Smith or Carbocoal Process

This is a process at present worked only in America by the International Coal Products Corporation. The Corporation has bought complete ownership of the process developed by C. H. Smith of New York, and has constructed plant at Irvington, New Jersey, and at South Clinchfield, Virginia, under the auspices of the U.S.A. Government, the latter plant commencing to operate in July, 1920, and having a capacity of 550 tons per day. Carbocoal has been made from lignites, coking, semi-coking and non-coking coals.

In this process the coal is subjected to a combination of low and high temperature carbonisation, the final product being a briquette of low volatile matter, whilst a high yield of oil and also of ammonia is obtained. An outstanding feature of the process is the continuous working of the primary retorts.

Outline of the Process

The coal, usually of a high volatile matter content and of a bituminous nature, previously crushed to pass a sieve of $\frac{3}{8}$ inch mesh, is carbonised at a temperature of about 480° C. with the formation of a high yield of low temperature tar,

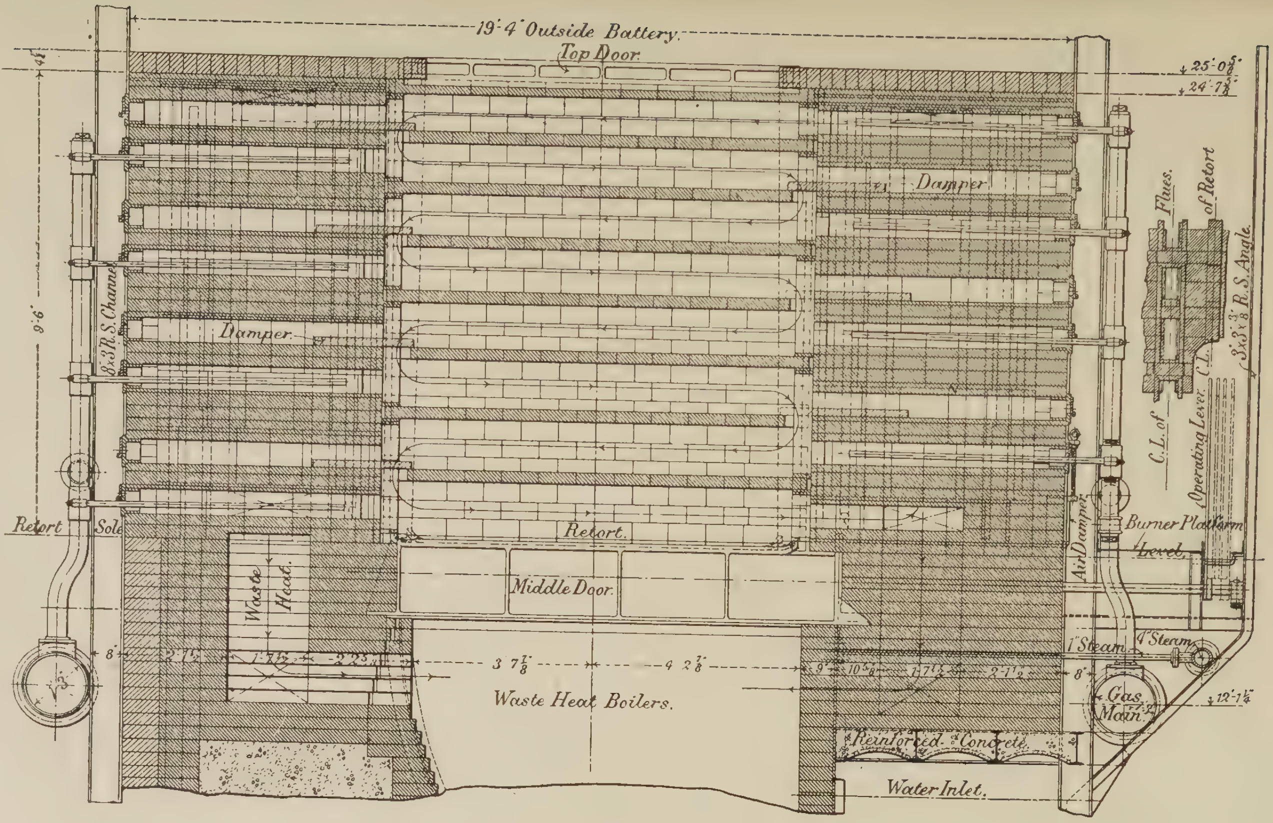

Fig. 6.—Coalite Process
Section through Retort Flues

and about 6,000 c. ft. of gas of high calorific value (650-700 B.Th.U's. per c. ft.), whilst the solid residue or semi-carbocoal, as it is termed, is a friable pulverulent material containing about 7-10 per cent. volatile matter. The next stage consists in grinding up the semi-carbocoal and mixing it with a certain percentage of pitch to act as a binding agent. After briquetting the material thus obtained, which now contains about 15 per cent. of volatile matter, the briquettes are subjected to the secondary or high temperature carbonisation at about 1000-1100° C., which drives off all but 3-4 per cent. of volatile matter, yielding a quantity of ammonia and thick tar, whilst the solid residue is obtained in the form of firm, hard briquettes, capable of withstanding transport and rough handling. The quantity of gas obtained per ton by the secondary distillation amounts to nearly 4,500 c. ft. of calorific value varying from 350-400 B.Th.U's. per c. ft. After the demands made by the plant have been met, there still remains a surplus of more than 2,200 c. ft. of gas.

THE PLANT

Throughout the process full advantage is taken of labour-saving devices, mechanical handling being adopted. The actual plant may for convenience be divided into four sections :—

(*a*) The primary retort plant.
(*b*) The briquetting plant.
(*c*) The secondary retort plant.
(*d*) Auxiliary plant.

(*a*) *The Primary Retort Plant*

The coal as received is delivered into a storage bin, and thence conveyed by means of a track hopper to the coal crusher, where it is reduced to the necessary degree of fineness. The crushed coal is then delivered by means of an elevator and belt conveyor to coal hoppers of eight tons capacity which automatically feed the primary retorts. The retorts (Fig. 7) are 7 ft. wide, 5 ft. high, and 19 ft. long, and have the shape of an inverted heart. They are built up of carborundum blocks with tongued and grooved joints specially packed with asbestos, whilst the ends of

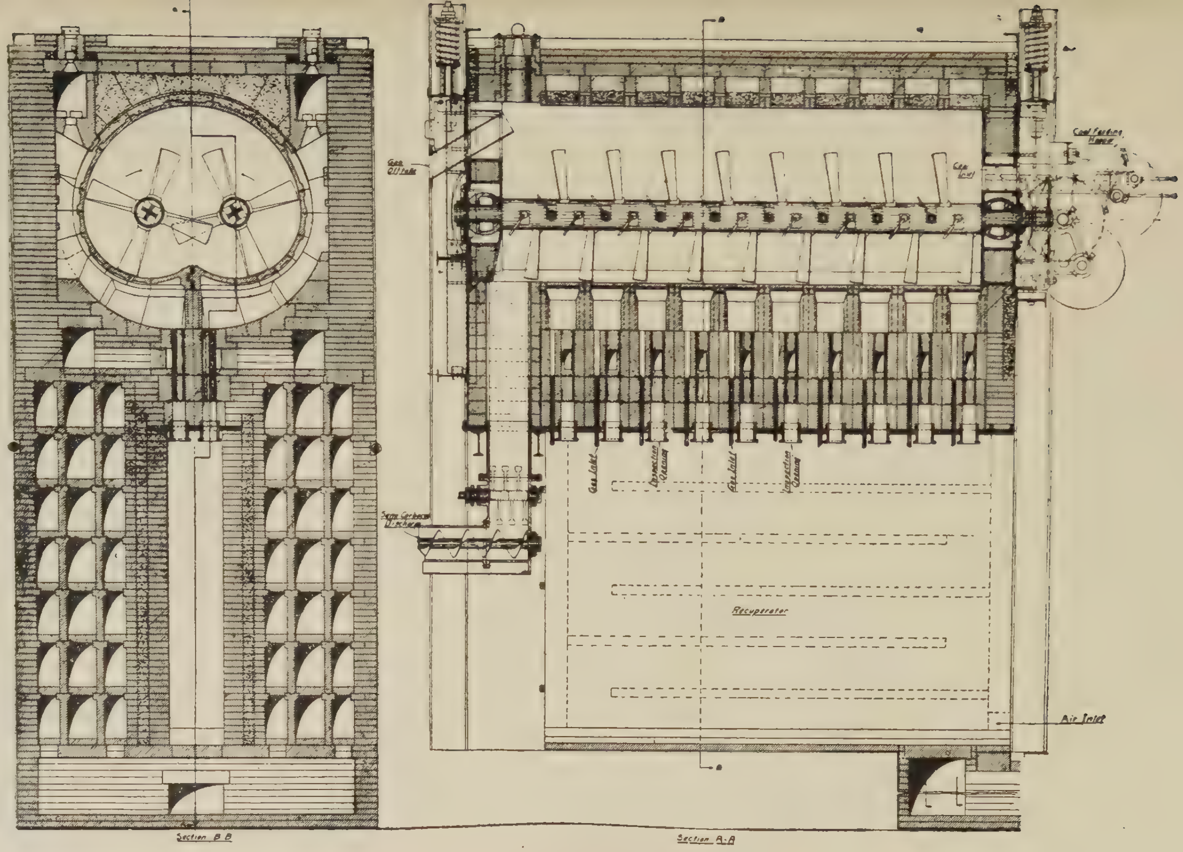

FIG. 7.—CARBOCOAL PROCESS.
PRIMARY RETORT.

the retorts are made of cast iron lined with fire brick. This type of retort has, so far, proved to be the most satisfactory both from the point of view of heat conducting and wearing capabilities. The coal is fed in at one end of the retort by means of a screw conveyor working in a closed tube, and is caused to pass through the retort by means of paddles attached to two shafts which revolve inside the retorts. These paddles, which have a radius of 2 ft. 3 ins. and a clearance between the retort wall of $\frac{3}{4}$ in., are bolted alternately on to either shaft. The shafts make eight revolutions per minute and require approximately 2 B.H.P. to drive.

A self-sealing device at the ends of the shafts prevents the leakage of the gas and tar from the retorts. The material is discharged at the other end of the retort by means of a revolving shaft fitted with arms to break up the product, so that no pieces are over 6 inches in size. These arms deliver the semi-carbocoal first into a water jacketed discharge hopper whence it passes by conveyors to the briquetting plant. The retort will deal with a variety of coals, and since, when operating, it is only about half full, there is plenty of room for intumescence, whilst uniform distillation is effected owing to the agitation of the coal by means of the paddles. The retorts are built in batteries of six, arranged in two groups of two batteries, that is to say, twenty-four retorts in all. The gas outlets are situated near the discharge end of the retort.

The heating is done by means of stripped gas, the burners being placed in flues surrounding the retort, whilst the air required for combustion is pre-heated by means of a recuperative system. Each retort has an output of about one ton per hour, working continuously, the coal passing through the stage of primary carbonisation in 2-3 hours, whilst the volatile products of distillation escape at the top of the retort by means of an ascension pipe, the volatile content being reduced from about 36 per cent. in the raw coal to from 7 to 10 per cent. in the resulting product.

The semi-coke discharged from the primary retorts, falls on to covered conveyors which pass along the ends of each battery, and is carried to storage bins situated at the briquetting plant.

(*b*) *The Briquetting Plant*

This consists of (1) a crusher, for breaking up the semi-carbocoal to below $\frac{1}{8}$ inch; (2) a mixer, in which from 8 to 10 per cent. by weight of liquid pitch is run and mixed with the coarsely powdered material; (3) a "fluxer," in which the mixture is treated with steam which thoroughly incorporates the material, and facilitates the operation of the briquetting press which is of the roll type. The raw briquettes produced then pass by means of a cooling conveyor to a revolving screen, which removes fines and returns them to the fluxer, whilst the briquettes are subsequently passed to a storage bin, ready for final carbonisation.

(*c*) *The Secondary Retort Plant*

This is constructed after the manner of an inclined horizontal gas retort, the retort being rectangular in shape and divided into three compartments, each containing two carbonising chambers, charged and discharged by means of gravity (Fig. 8). During the secondary distillation, which occupies about six hours, there is a marked shrinkage in the volume of the briquette, and a corresponding increase in density. The capacity of the secondary retorts is about 60-75 tons of raw briquettes per day.

The secondary retorts are built in batteries, each battery generally consisting of six retorts. Each retort is approximately 12 feet wide, 21 feet long, and 26 feet high at the discharge end, and these retorts are fitted with a similar recuperative system for pre-heating the air to that employed in the primary retorts. Each retort is provided with a separate hydraulic main and tar catch tank, and from here the gas is passed on to the auxiliary plant for the recovery of tar, ammonia, and light oil.

(*d*) *Auxiliary Plant*

The auxiliary plant consists of the usual by-product plant, in which the tar oils and ammonia are recovered. The gases from the primary and secondary retorts are mixed and passed back, through suitable storage and stand-by plant to the gas mains feeding the primary and secondary retorts. The sulphuretted hydrogen is not removed from the gas in this auxiliary plant.

PRODUCTS OF THE SYSTEM*

The final products obtained per ton of coal, using a bituminous coal of high volatile matter (about 35 per cent.), average:—

(1) 65 to 70 per cent. briquettes.
(2) 10,000 cubic feet gas—calorific value 550 B.Th.U's.
(3) 20 to 24 lbs. ammonium sulphate.
(4) 30 gallons of tar.

In addition, approximately 2-3 gallons of light oil are obtained by stripping the gas. Carbocoal tar gives upon distillation the following fractions:—

	°C.	Percentage.
Light Oil	0-170	4·66
Middle Oil	170-230	13·67
Creosote Oil	230-270	11·57
Heavy Oil	270-360	27·01
Pitch and Loss		43·09

Approximately 35 per cent. of fraction 170-360° consists of tar acids, whilst the pitch obtained is used principally as a binder for the briquettes.

The fractionation and working up of the tar is also carried out, and the table below indicates the yield of by-products from 1,000 tons of coal.

Coal	1 000 tons
Carbocoal	700 tons

Analysis.

	Raw Coal.	Carbocoal.
Moisture	0·72	1·84
Volatile Matter	35·01	2·75
Fixed Carbon	57.23	85·64
Ash	7·04	9·77
Sulphur	0·63	0·52

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* Private communication.—Lieut.-Col. C. A. Grenfell.

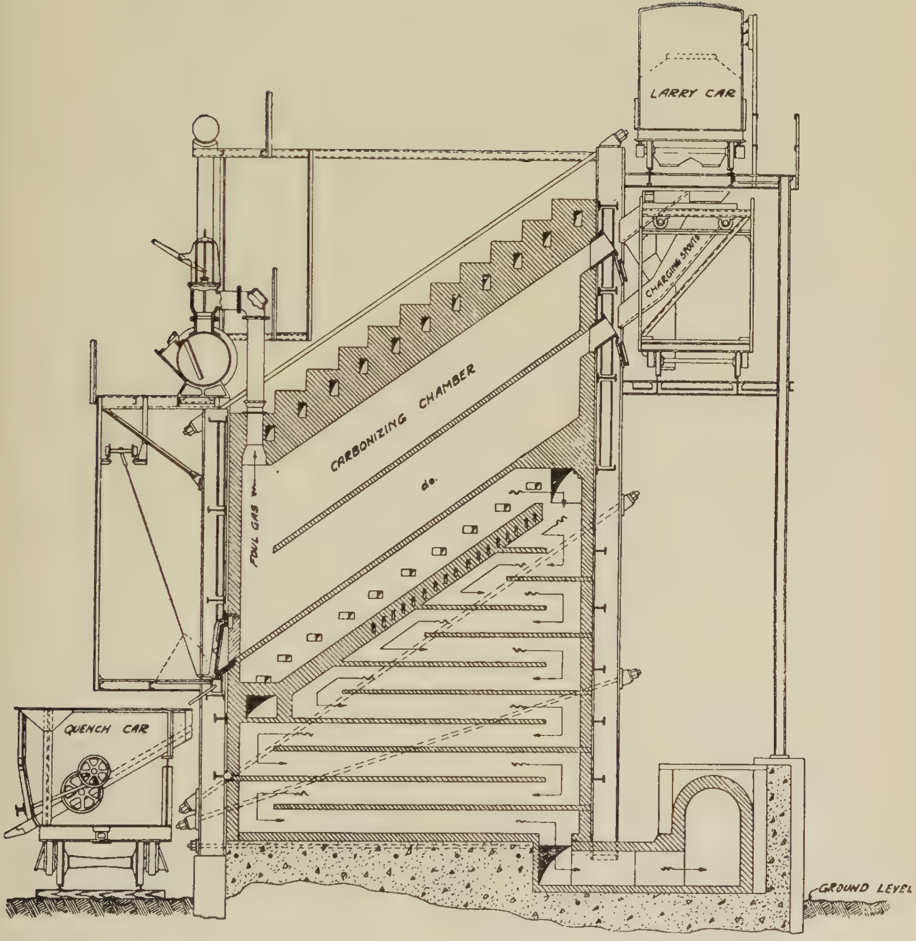


FIG. 8.—CARBOCOAL PROCESS
CROSS SECTION THROUGH SECONDARY RETORT

Ammonium sulphate	20,000-25,000 lbs.
Motor Spirit	2,000- 2,500 gallons.
Crude tar acids, chiefly cresylic	4,000- 4,500 ,,
Neutral oils	3,200- 3,800 ,,
Creosote oils	3,500- 5,000 ,,
Heavy creosote oil	5,000- 8,000 ,,
Surplus gas (550 B.Th U's. per c. ft.)	2,000,000 c. ft.

CARBOCOAL

Carbocoal is a dense compact free-burning and smokeless fuel and is marketed in briquette form, standing transport without disintegration. Tests carried out by the U.S. Navy Department show that when burnt under a Babcock and Wilcock boiler, very satisfactory results were obtained, the tests indicating that one pound of carbocoal evaporated 9·09 lbs. of water from and at 100° C. as against 9·59 lbs. for the original coal from which it was produced. The fuel has also been employed for marine and locomotive services, domestic uses in furnaces, stoves, etc., and in drying ovens, and gas producers, etc.

The following figures indicate the proximate analysis of carbocoal together with that of the coal from which it was derived :—

Coal.

Volatile Matter.	Fixed Carbon.	Ash.	Sulphur.	B.Th.U's.
32·50	63·70	3·80	0·79	15,182
33·80	59·99	6·21	1·91	14,401
36·90	60·05	3·05	0·65	14,587
39·70	57·44	2·86	0·66	14,600
40·40	53·60	6·00	2·54	13,807

Carbocoal.

Volatile Matter.	Fixed Carbon.	Ash.	Sulphur.	B.Th.U's.
2·38	91·71	5·91	0·60	13,668
2·16	88·61	9·23	1·31	13,168
4·88	88·49	6·63	0·52	13,606
5·30	87·99	6·71	0·55	13,799
3·21	86·81	9·98	1·98	13,087

All results calculated on a dry basis.

The Maclaurin Process

The Maclaurin process has been developed by Maclaurin working under the auspices of a sub-committee of the Glasgow Corporation Gas Committee upon experimental plant erected at Port Dundas and at Grangemouth. The plant was primarily erected with a view to the production

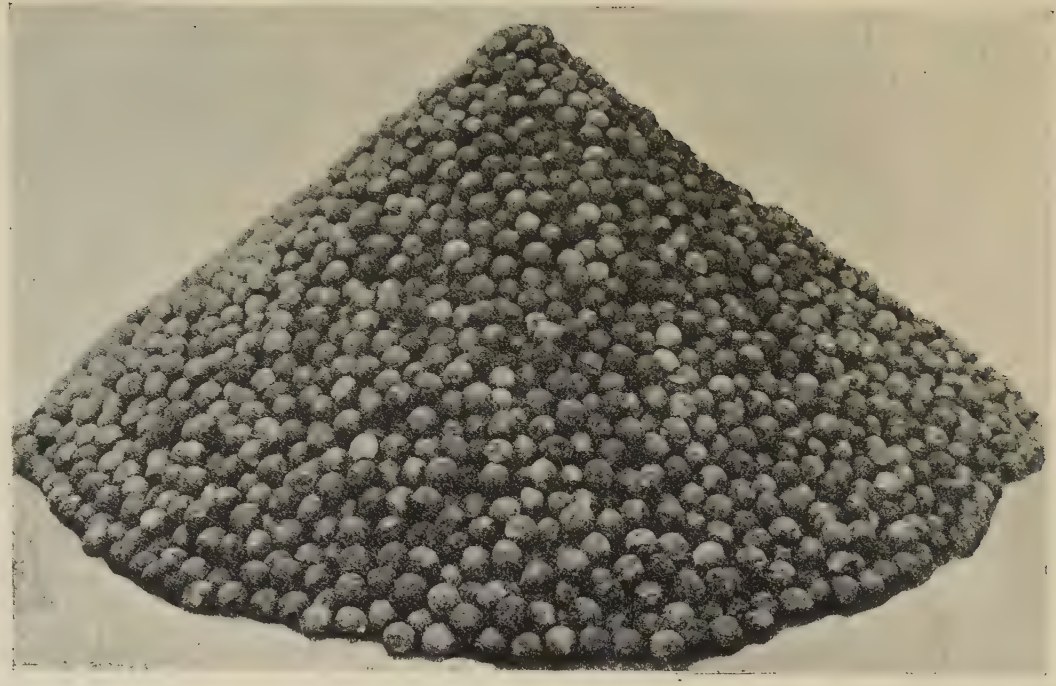


FIG. 9.—CARBOCOAL.

of a smokeless fuel and illuminating gas. The process is now controlled by Maclaurin Carbonisation Ltd., and investigations are proceeding upon the tar and liquors under the supervision of a company formed for this purpose and termed the Scottish By-Products Limited.

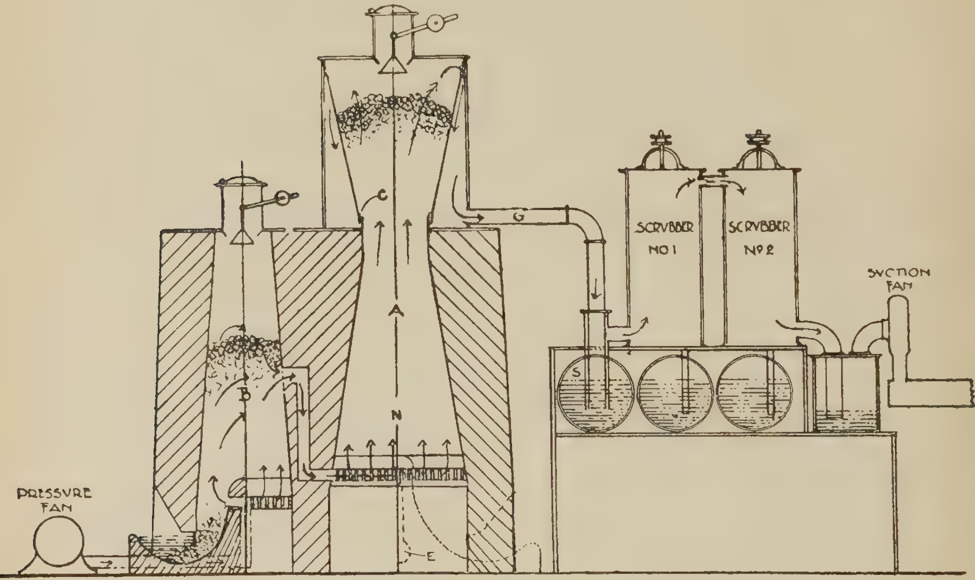


FIG. 10.—MACLAURIN PROCESS.

A—Main producer. B—Supplementary producer. C—Annular collar. E—Inlet for air and steam. G—Outlet pipe. S—Seal tank.

OUTLINE OF PROCESS

In the Maclaurin process the carbonisation of the coal is effected by the sensible heat of crude producer gas. In the first experiments undertaken by Maclaurin two producers, built adjacent to one another, were employed, as shown in Fig. 10. Gas from the smaller producer B was utilised for the carbonisation of the coal passing down the larger producer A. Producer A was of special construction, being made considerably higher whilst retaining the width of the ordinary producer. The special feature of producer A, however, consisted in the provision of an annular collar C, placed a short distance from the top of the producer and so designed that the tar and oil condensing on the sides of the top of the producer were trapped in the collar and run off to the seal tank S, thus preventing decomposition of the oils, and the consequent "sticking up" of the producer.

Modifications in the plant have since been introduced, and at the present time only one producer is employed.

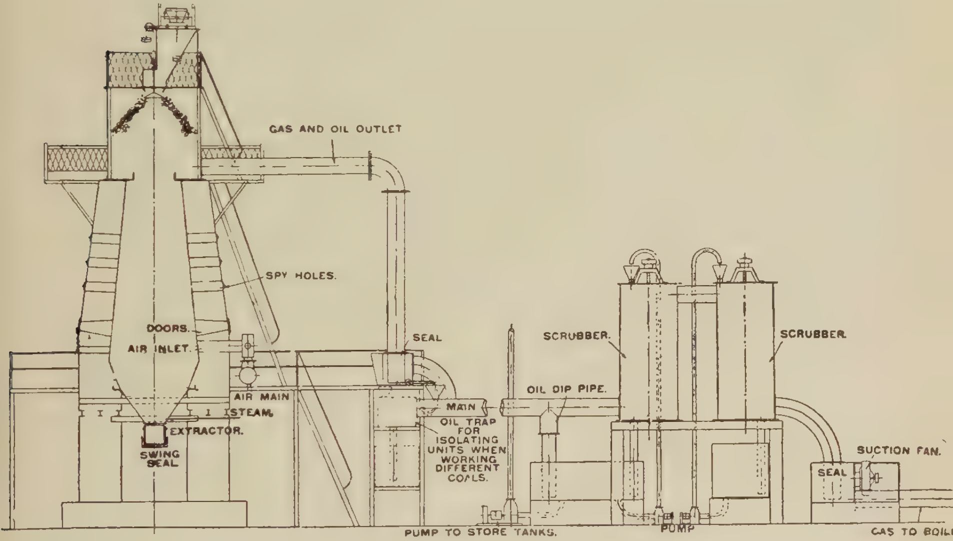


FIG. 11—MACLAURIN PROCESS

In general proportions, this producer or retort is similar to the blast furnace, but on a smaller scale, the height being about 40 ft. and the width at the combustion zone 8 ft. It is provided with a collar to trap oils and tar as in the plant mentioned above, and a swing seal is arranged at the base of the producer for the extraction of the coke produced.

Fig. 11 shows the arrangement of the present plant, in which the patent collar for the trapping of the tar and oils is clearly shown. By the provision of this collar, it is claimed that the oils and tars produced suffer a minimum of decomposition, the coal being submitted to a gradually increasing temperature, the tars and oils being obtained without subjection to a higher temperature than that at which they are evolved from the coal. After passing the combustion zone, in which a small quantity of the fuel is consumed, the semi-coke is allowed to cool in its passage through the lower end of the producer, and is ejected by means of the swing seal already referred to. By suitably controlling the air blast, it is claimed that either a metallurgical coke or a fuel suitable for domestic consumption can be produced, whilst, if desired, the whole of the coal can be gasified as in an ordinary producer.

It is stated that coking and non-coking coals have been successfully carbonised in this producer, and that owing to the gradual heating up of the coal, except in the case of very strongly coking coals, no " sticking up " of the producer has been encountered. Little or no binding together of the coal takes place, although the semi-coke obtained is considerably harder than the coal from which it is produced, resembling gas coke in this respect, but being black in contrast to the grey metallurgical coke produced by the plant when working for this product.

The following details are given by Maclaurin (Paper before the S. Wales Inst.Eng., Cardiff, April 20th, 1922) of the oil, gas and ammonia yields :—

Nature of Oil

The oil contained no benzene, naphthalene, or anthracene, and practically no light oils. The distillates were characterised by a high percentage of phenolic bodies, the lighter distillates containing up to 50 per cent. of phenols, particularly cresols and xylenols. The distillates above 270° C. contained a large percentage of solid paraffins. The crude oil as obtained was " a brown waxy oil," which could be directly utilised as a fuel oil.

Gas

The gas made over a period of 24 hours was of the following composition :—

	Percentage.
CO_2	6·2
C_nH_m	nil
O_2	0·6
CO	16·0
CH_4	13·0
H_2	16·1
N_2	48·1

Gross calorific value 247 B.Th.U's. per c. ft.

The gas was characterised by the absence of hydrocarbons other than methane, due to the oils not suffering decomposition, and was obtained free from masses of tar.

Ammonia

The ammonia yield was approximately 24 lbs. of ammonium sulphate per ton of coal carbonised when semi-coke was being manufactured, and the ammoniacal liquors were practically free from ferrocyanide and sulphocyanide.

Yields per Ton of Coal

From one ton of coal of 35 per cent. volatile matter, 7·7 per cent. moisture and of calorific value 12,000 B.Th.U's. per lb. the following yields were obtained :—

Coke

8·05 cwt. of large coke (smokeless fuel) of calorific value 12,600 B.Th.U's. per lb.
1·16 cwt. of Smithy Char. of calorific value 12,196 B.Th.U's. per lb.
0·76 cwt. of Peas of calorific value 11,283 B.Th.U's. per lb.
0·99 cwt. of Breeze of calorific value 9,203 B.Th.U's. per lb.

10·96 cwts. Total.

Tar and Gas

15·6 gallons (1·44 cwt.) of oil, moisture free, of calorific value 16,600 B.Th.U's. per lb.
27,731 c. ft. of gas of calorific value 247 B.Th.U's.

The following table shows analyses of cokes obtained by the Maclaurin process from various coals (J.Soc.Chem.Ind. 1917. 36. 620) :—

	Water.	Volatile Matter.	Fixed Carbon.	Ash.
	%	%	%	%
Cannel Coal . . .	10·70	30·72	46·51	12·17
Residue from Cannel Coal .	...	...	...	18·00
Cadder Coking Coal . .	10·40	32·99	50·44	6·19
Dried Smokeless Fuel from Cadder Coking Coal .	...	4·77	86·71	8·52
Greenhill Coal . . .	12·69	33·09	50·63	3·85
Dried Smokeless Fuel from Greenhill Coal . .	...	3·9	...	...
Coke from Horizontal Retorts for comparison purposes .	...	4·30	86·40	9·30

Maclaurin noted the small amount of volatile matter present in the cokes obtained from this process, and expressed the opinion which has later been borne out by

Evans and Sutcliffe that ease of ignition of a semi-coke was not dependent upon the volatile matter which it contained. Evans and Sutcliffe have demonstrated that ease of ignition is dependent rather upon the structure of the coke, the distribution and size of the air cells, together with its non-graphitic nature, being the criteria.

Semi-cokes produced by the Maclaurin process are stated to be excellent for steam raising purposes, and values of its efficiency, calculated by Playfair's formula, are as follows (Iron and Coal Trades Review, 1921. 102. 848) :—

Coal.	Percentage Composition.	Lbs. of Water Evaporated.
Moisture	5	—
Volatile Matter	35	1·08
Fixed Carbon	55	7·15
Ash	5	—
	100	8·23

Smokeless Fuel from above Coal.	Percentage Composition.	Lbs. of Water Evaporated.
Volatile Matter	4	0·124
Fixed Carbon	87	11·310
Ash	9	—
	100	11·434

The L.M.N. Process

The L.M.N. process is owned and controlled by Messrs. Bryan Laing, F. D. Marshall and Harald Nielsen, of 100 Victoria Street, London, S.W.1, hence the name.

Primarily it has been designed to operate in cases where producer gas is used for firing steel furnaces, in order to increase the overall efficiency of producer gas manufacture, permitting at the same time the recovery of by-products.

Normally, in order to utilise the sensible heat of producer gas as it passes from the producer (at a temperature of about 780° C.) the producer is built as close as possible to the furnace in which the gas is to be used, a system which presents a number of drawbacks.

The producer occupies space which is valuable in a working area, whilst restricting the normal furnace work in so far as fuel has to be transported to the producer and ash or clinker taken from the working area, and the working of the producer must be synchronised with the working of the furnace if full advantage is to be made of the sensible heat of the producer gas.

To overcome these drawbacks Nielsen has devised the above process.

It is stated that a plant is now in course of erection for the Carbon Products Company of India.

In the consideration of this process it must be clearly recognised that primarily it has been designed to meet a particular case, and no claims are apparently made either for its application to the sole production of a smokeless fuel or for the manufacture of the gas for power production.

OUTLINE OF PROCESS

The plant, designed, in this case, to deal with 100 tons of coal per day, is shown diagrammatically in Fig. 12.

The essential feature of the process consists in the utilisation of a rotary retort of special construction for the primary carbonisation of the fuel, Fig. 13.

This retort consists of a steel shell 90 ft. long and 7 ft. to 9 ft. internal diameter, having near its larger end an annular belt 14 ft. in diameter. It is lined with 9 in. firebrick and 3 in. insulating brick, and the steel shell is insulated outside so that the radiation losses are reduced to a minimum. The retort is mounted on friction rollers and is geared to rotate, being so inclined that its larger end and the annular belt are slightly lower than the smaller end. Raw coal is fed into the smaller end from a bunker by means of a screw conveyor, and passing down the rotating retort, meets the counter stream of hot gas from a producer situated at the other end, and in its passage undergoes carbonisation. The carbonised coal is received in the annular belt from which it is discharged by means of a discharging door operated by suitable mechanism, whilst the now enriched producer gas carrying the volatile products from the coal passes out to the usual by-product recovery plant. The supply of raw coal into the retort is governed by an automatic measuring device.

The producer is specially designed to operate with the rotary retort.

A portion of the semi-coke produced is used in the producer, the gas from which passes through the rotary retort, whilst the balance of the semi-coke is utilised in other producer plant, the sensible heat of the gas produced by this plant being recovered in tubular waste heat boilers and tubular feed water heaters linked up to the hot gas outlets. By mixing the producer gas from these producers with the rich gas obtained from the rotary retort, the calorific value of the resultant mixture, after scrubbing, is brought up to about 180 B.Th.U's. per c. ft. at standard pressure and temperature. It is further claimed that the sensible heat of the producer gas from the semi-coke gasified in the primary producer and in the auxiliary producers is not only sufficient to carbonise the raw coal in the rotary retort, but by means of the waste heat boilers provides sufficient steam to operate the whole of the producer plant.

The following data are given by Nielsen of the performance of the plant (Engineering, 1922. 113. 347):—

Coal used;

Proximate Analysis:

	Per cent.	
Moisture	2·80	Heating value round 6,330 kg. cal. per kg.
Volatile Matter	31·10	
Fixed Carbon	53·70	
Ash	12·40	
	100·00 = 11,400 B.Th.U's. per lb.	

Ultimate Analysis of Raw Coal:

	Per cent.	
C	68·00	
H_2	4·00	Net H_2 = 2·80 per cent.
O_2	9·70	
N_2	1·30	
S	1·80	
Ash plus Moisture	15·20	
	100·00	

"By the low temperature distillation of this coal by means of the sensible heat of producer gas in the rotary retort a semi-coke of the following proximate analysis is produced:—

	Per cent.	
Moisture	1·90	Heating value about 6,400 kg. cal. per kg.
Volatile Matter	11·50	
Fixed Carbon	70·70	
Ash	15·90	
	100·00 = 11,500 B.Th.U's. per lb.	

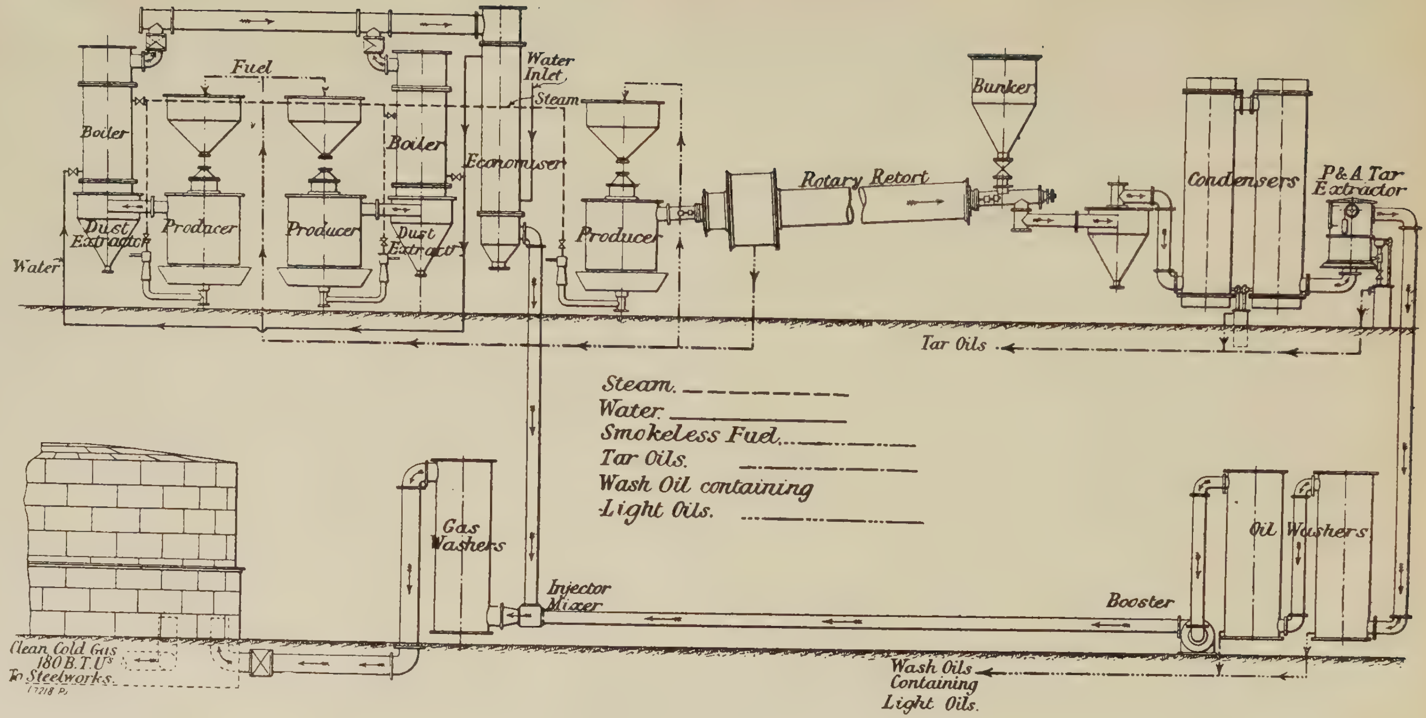


FIG. 12—L.M.N. PROCESS
GENERAL LAYOUT OF PLANT

"The coke is cooled down below the igniting-point in the free atmosphere by being kept in contact with an inert gas (producer gas) in a cooling chamber fixed to the retort.

NOTE.—The moisture percentage in analysis was due to the exposure to the weather.

Ultimate Analysis of Semi-Coke:

	Per cent.	
C	71·20	
H_2	2·90	Net hydrogen = 2·30 per cent.
O_2	4·90	
N_2	1·50	
S	1·70	
Ash plus Moisture	17·80	
	100·00	

"Gasifying the semi-coke in a producer of the above-described type, a producer gas of the following composition is obtained:—

	Per cent.
CO_2	6·00
O_2	0·40
CO	25·50
H_2	13·50
CH_4	2·60
N_2	52·00
	100·00

Average Composition of Crude Tar Oils

	Per cent.	Specific Gravity.
70 deg. to 180 deg. C.	4·75	0·80
180 deg. to 230 deg. C.	20·00	0·87
230 deg. to 270 deg. C.	14·50	0·97
270 deg. to 320 deg. C.	24·00	1·01
Total	63·25	

Residue: Hard pitch and loss = 36·75 per cent. by dry distillation
Neutral oils soluble in petrol, 52 per cent. by volume.
Phenol oils soluble in petrol, 20 per cent. by volume.
Insoluble in petrol, 28 per cent. by volume.

"The neutral oils show no sign of decomposition at 400° C.

Heat recovered in tubular waste heat boilers, linked up to hot gas outlet at producers, gasifying balance of semi-coke:—

Temperature of hot gas, entering boilers, 560 deg. C.
Temperature of hot gas, leaving boilers, 250 deg. C.
Amount of heat utilised in steam raising: 193,000 kg. cal., corresponding to about 370 kg. steam raised from and at 100 deg. C. at 4 atm. pressure.
Net steam raising efficiency: About 60 per cent.

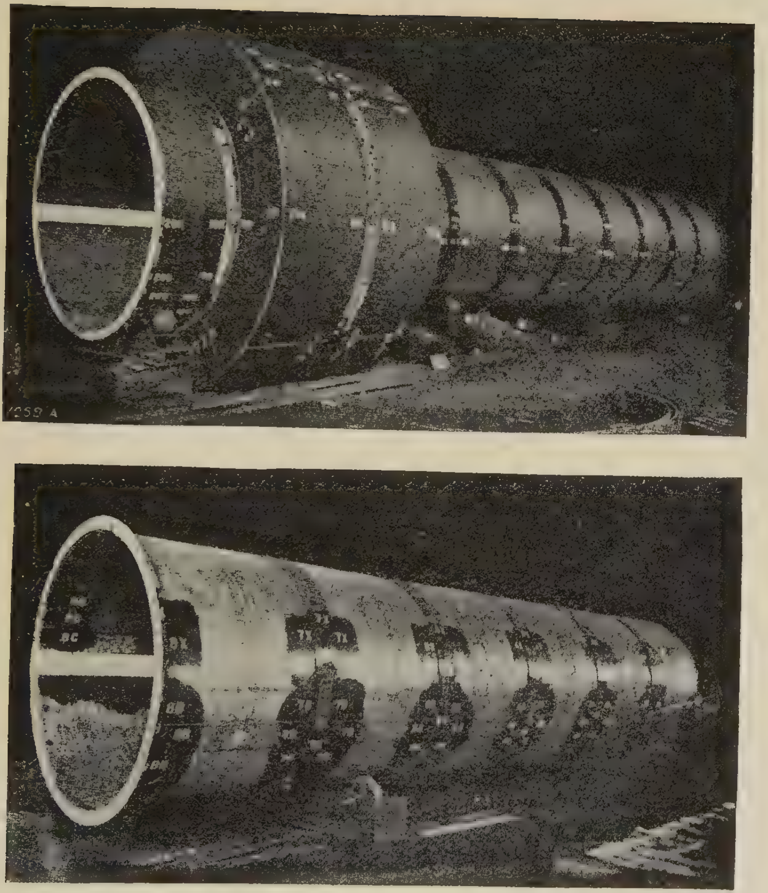


Fig. 13.—L.M.N. Process
Rotary Retort

"The above amount of steam corresponds closely to the total steam requirements of the operating producers.

Utilising the sensible heat of the producer gas as it leaves the waste heat boilers at 250° C., in tubular feed-water heaters, the feed-water is raised to boiling-point, so it will be clear that as far as steam requirements are concerned, the plant is self-contained and does not require any outside supply for the process.

Total net thermal efficiency of combined processes:—

	Kg. Cal.
In.	
1 ton of raw coal	6,333,000
Out.	
Gas, net heating value	4,700,000
Tar oils	729,000
	5,429,000

Efficiency $\frac{5,429,000}{6,333,000} = 85\cdot6$ per cent.

"NOTE.—Regarding sulphate recovery.

As the producers are not run under by-product conditions, that is to say, for the maximum yield of sulphate, it is very doubtful whether it would pay to recover the small amount involved, a maximum of 15 lb. to 20 lb. per ton of coal treated by the combined process. If the gas was not specifically required for steel furnaces, but for power plant purposes, the aspect would naturally become quite different."

The Pure Coal Briquette Process

The Pure Coal Briquette process is controlled by Messrs. Pure Coal Briquettes Ltd., a company formed by the late Lord Rhondda, and having Messrs. Sutcliffe, Speakman & Co. Ltd. of Leigh, Lancashire, as its constructional and consulting Engineers.

The development of the process is the result of research work undertaken by E. C. Evans, late head of the Rhondda Research Laboratories, Llwynypia, Glamorganshire, and E. R. Sutcliffe of Messrs. Sutcliffe, Speakman & Co. Ltd., and the process marks a distinct step in the progress of low temperature carbonisation methods and in the knowledge which we possess of the nature of smokeless fuels, Prior to the investigations of Evans and Sutcliffe, it was generally assumed that the ease with which low temperature carbonisation coke would ignite and continue to burn was dependent largely upon the presence in the coke of a certain amount of volatile matter (approximately 10 per cent.).

From the microscopic study of the fuels prepared by this process it would appear that the ease of ignition of coke depends upon the physical structure of the coke rather than upon its chemical composition. Cokes which possess a structure in which the air cells are minute and evenly distributed throughout the mass, and which are not covered with a graphitic film, ignite easily, in contrast to graphitic cokes in which the cells are comparatively large and in which fairly large, solid masses occur. The cokes prepared by this process appear to possess a particularly even structure in which air cells and carbonaceous matter are finely distributed throughout the mass, and further, this coke is not covered with a graphitic film as in the case of gas works and foundry cokes.

Other factors, such as volatile content, may certainly affect the ease of ignition of a coke, but the physical structure as outlined above appears to play the predominating part.

Outline of the Process

The essential feature of the Pure Coal Briquette process consists in the preparation of the coal prior to carbonisation. Although a special type of retort has been designed, carbonisation may be carried out in existing plant such as gas-works and coke-oven plants.

As in all carbonisation processes it is necessary in this process to employ clean coal, in order to obtain a coke of reasonable ash content. Washery plant of standard type coupled with a froth flotation installation for the cleaning of fine coal is advocated.

The washed coal passes to dryers, in which the moisture content is sufficiently reduced to admit of the coal being subsequently pulverised. The dryer usually recommended with this system is the " Static " dryer, which is shown in Fig. 14. By means of screw conveyors, the coal is then passed to ball or tube mills (Fig. 15) in which the coal is pulverised so that the whole will pass through a 1/30 mesh sieve, being at the same time intimately blended with a predetermined quantity of previously carbonised material, coke breeze or coal of a suitable caking power, so as to obtain an ultimate product which will not swell excessively on carbonisation.

From the grinding plant the coal is again passed by screw conveyors to briquetting machines of special design in which it is submitted to a pressure of about 10 tons per sq. inch. Owing to the fineness of division of the coal and the high pressure to which it is submitted, the resulting briquettes are sufficiently hard to withstand transport and weathering, being stated to be harder than lump coal, and comparable with the average briquette made with a binder such as pitch. The briquette presses in use are modified types of the Sutcliffe Speakman " Emperor " press, and " Ovoid " presses of special design (Fig. 16).

Subsequent carbonisation at high or low temperatures of the coal briquettes prepared in this manner yields a smokeless fuel of excellent quality, and dependent upon the degree of pulverisation and upon the temperature of carbonisation, cokes varying from domestic fuel to a special blast furnace fuel have been produced.

On the other hand the best domestic fuel is obtained by submitting the briquettes to carbonisation at gradually increasing temperatures, and Messrs Pure Coal Briquettes Ltd. have designed a special type of retort for this purpose.

This consists essentially of a vertical retort fitted with suitable charging and discharging mechanism, the charge being heated by a stream of superheated gas, obtained from a previous retorting, and being passed, prior to superheating, to by-product recovery plant in which it is stripped of ammonia, light spirit and tar.

The superheaters are placed on either side of the retort, and are heated either by fuel oil or gas obtained in the process. The construction of the retort and the fact that it is internally heated, admits of the erection of retorts of practically any capacity—individual retorts at present being designed to carbonise 250 tons per retort per day of 24 hours,

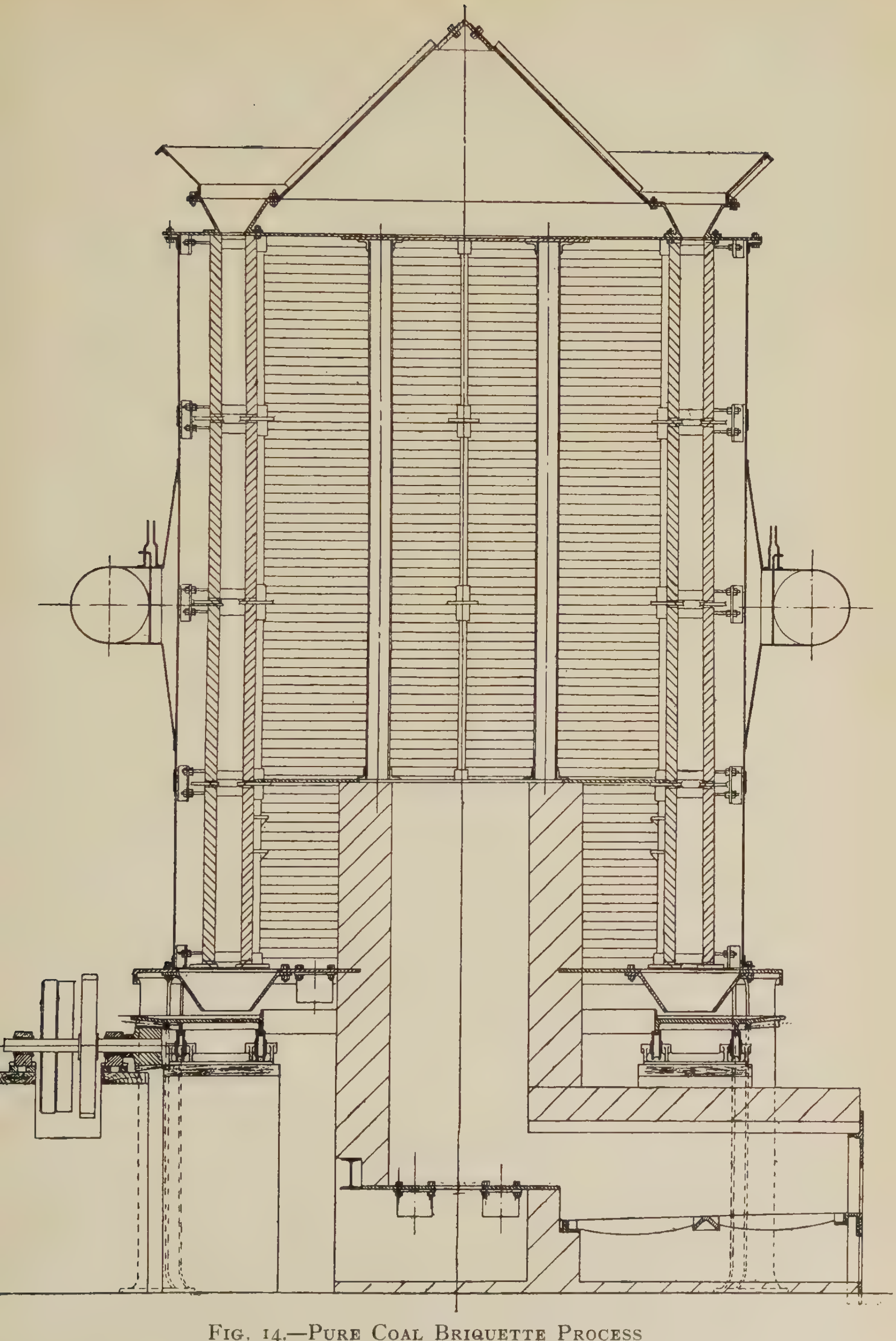


Fig. 14.—Pure Coal Briquette Process
Static Dryer

The layout of plant necessary to carbonise 1,000 tons per 24 hours is shown in Fig. 17, facing page 122.

The temperature of the stream of gas issuing from the superheater and passing through the charge in the retort can be easily regulated, and the coal is gradually raised from a temperature of approximately 500° C. to the maximum temperature of 1000° C.

Under such conditions the volatile content of the coal is expelled at the minimum temperature, and there is practically no cracking of the light spirit and tar, of which a maximum yield is obtained.

On the other hand the tar is essentially a low temperature tar and, at the present time, its most advantageous outlet appears to be as fuel oil. This method of retorting suffers, in common with other low temperature carbonisation processes, from our paucity of knowledge upon the constitution of low temperature tar, and the consequent working up of such tar to the fullest advantage.

The yield of tar, working on bituminous coals, is from 15 to 25 gallons per ton of coal carbonised, whilst a yield of from 3 to 5 gallons of light spirit per ton is stated to be obtained, dependent upon the character of the coal treated.

The nature of the coke product varies according to the methods of working. The coke is obtained from the retort in a form only slightly different in appearance from that of the briquette prior to carbonisation, being approximately the same size as the briquette or slightly smaller and suffering fracture to a small extent with the production of breeze or fine coke. The coke is hard and has a density approximating to that of anthracite. On ignition, owing to the fact that it is permeated with minute air cells or pores, it will burn until practically the whole of the carbonaceous matter is consumed, resembling charcoal in this respect. On the other hand, coals vary in their degree of combustibility, some burning completely to ash, whilst others leave a residue containing a considerable amount of carbonaceous matter (cinders). Cokes obtained from this process are stated to have been used satisfactorily in anthracite stoves and gas producers, and in open domestic grates they give a pleasant, very hot fire with little flame. For the special blast furnace

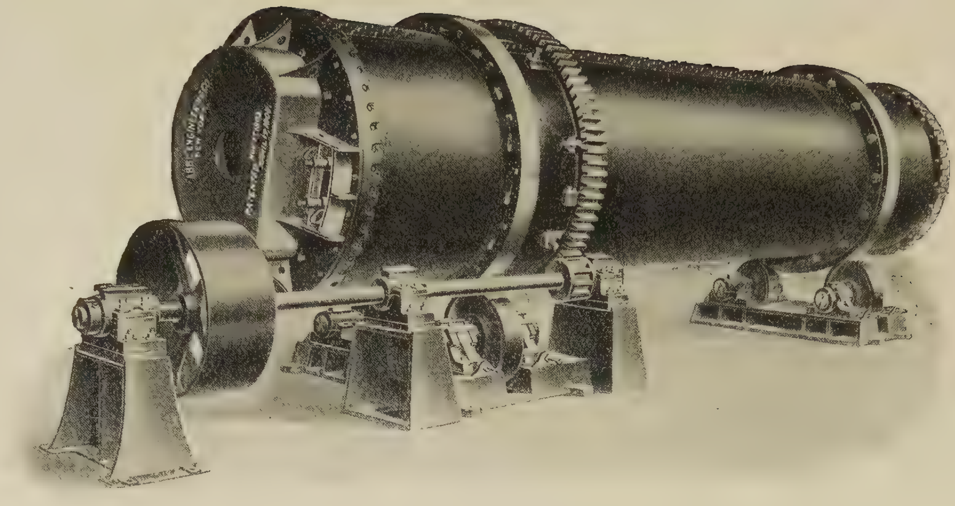


Fig. 15.—Pure Coal Briquette Process
Tube Mill

coke prepared by carbonising the briquettes in coke ovens many advantages are claimed. Briefly these are as follows :—

1. Charcoal furnaces have a considerably lower carbon consumption than coke fired furnaces, and as this special coke possesses properties very similar to charcoal, it is hoped that the use of this fuel will effect a saving of from 2 to 3 cwt. of coke per ton of pig iron produced.
2. The density of the coke being greater than that of furnace coke, a greater space will be available for ore and flux, and consequently the capacity of the furnace will be materially increased.
3. Owing to the active nature of the coke and its comparative hardness, it will retain its shape down to the oxidising zone in the furnace and be rapidly consumed there, resulting in a very intense concentration of heat, at the point at which it is most required.

An analysis of such coke showed the following composition :—

Fixed Carbon	84·6 per cent.
Volatile Matter	1·3 ,, ,,
Ash	10·6 ,, ,,
Moisture	3·5 ,, ,,
* Sulphur	1·9 ,, ,,

Evans and Sutcliffe make a further claim with regard to this process, stating that owing to the porous nature of the briquettes, a maximum yield of ammonium sulphate per ton of coal carbonised is obtained, exceeding the average yield in gas works practice by 50 per cent.

For example a coal containing 1·50 per cent. of nitrogen gave a coke containing 1·46 per cent. of nitrogen when carbonised in the usual way in a gas retort, whereas the same coal after preliminary pulverisation and briquetting, and carbonising under identical conditions gave a coke contain-

---

* NOTE.—Dependent on the sulphur content of coal carbonised.

ing only 1 per cent. of nitrogen. In small scale plant yields of ammonium sulphate per ton of coal carbonised have consistently been 50 per cent. higher than those obtaining in normal practice.

From tests carried out on pure coal briquette coke, it would appear to be an excellent fuel, not only for domestic use, but for practically all industrial purposes, and provided that the process can be worked economically it promises to take us a great step towards the realisation of a smokeless England.

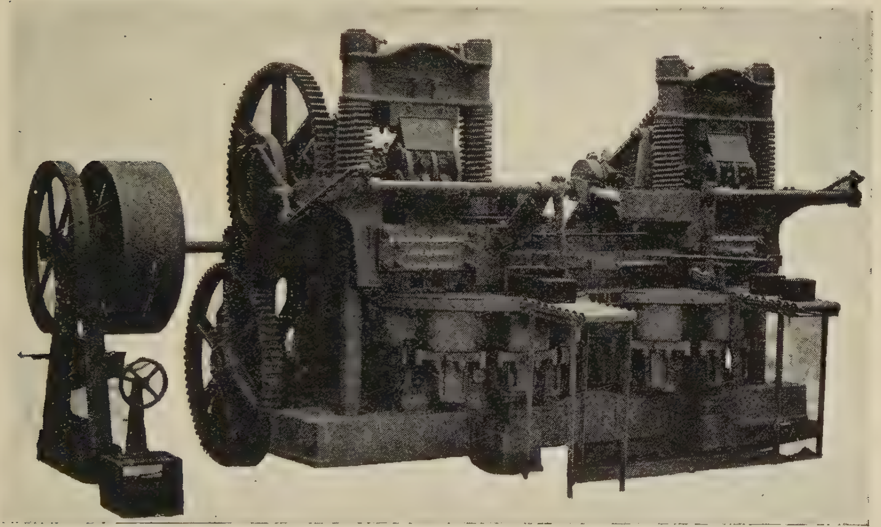


FIG. 16.—PURE COAL BRIQUETTE PROCESS
EMPEROR PRESS.

It has been found impossible in a book of this size to treat of all the processes proposed for the low temperature carbonisation of coal. The following, however, are also of interest, some from the historical standpoint and others in serving to show further the lines upon which the problem has been attacked.

Since the feature of these several processes centres in the construction of the retort, descriptions of the various types of retort only are given. A consideration of these processes serves to emphasise the point previously made, that the solution of the problems attendant on the carbonisation of coal at low temperatures has been mainly sought for by the exercising of mechanical genius, rather than by the exercise of chemical investigation into the nature of the coal substances.

Two processes stand out in relief, namely the Pure Coal Briquette process, which is based on the physical pretreatment of the coal, and that advocated by S. Roy Illingworth. The Illingworth process is given in the concluding pages of this chapter, and can, perhaps, be described as a process which has originated purely from chemical investigation.

The Del Monte Process

The Del Monte process was designed to work upon a continuous system, the evolved gases from the treated material being used as a medium for transferring heat to the material to be treated, such heat being supplied by a small producer placed below the retort. Fig. 18 is a diagrammatic sketch illustrating the process.

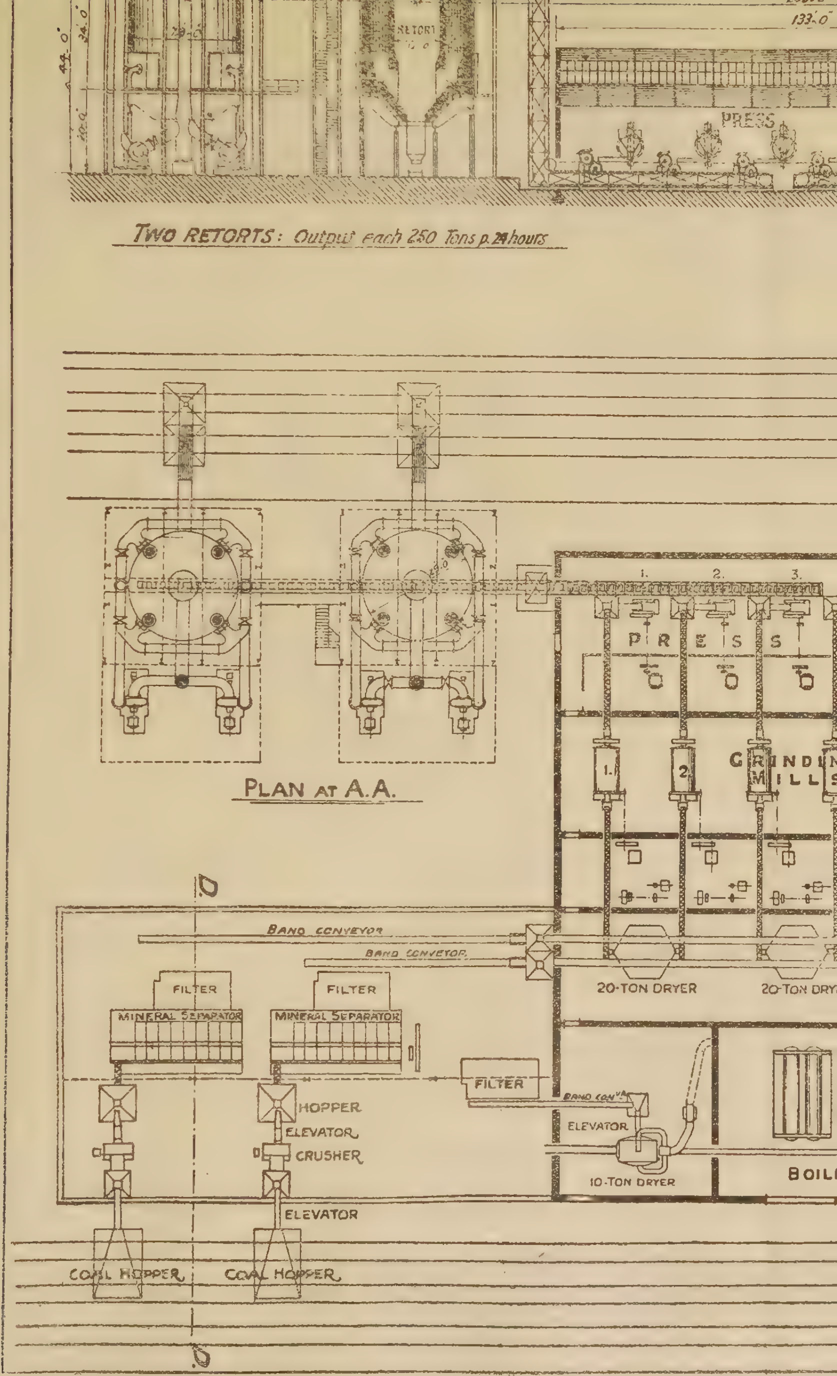
The retort A is filled with the material to be carbonised, and is heated by means of the producer B. When the volatile matter commences to be evolved from the coal, it is passed through the usual condensers, tar scrubbers, and ammonia recovery plant to the gas holder G, and from there returns to a tubular reheating system placed in the flues of the retort, whence it returns to the retort, being introduced at the base through a suitable diffuser, and passing continuously through the same cycle of operations. The coke is withdrawn at the base of the retort, the coal or other matter undergoing treatment being introduced at the top.

Results obtained by the Del Monte process are given by F. M. Perkin (J.Roy.Soc.Arts, 1915. 63. 859) as follows :—

Scottish Cannel Coal.

Moisture	7·30 per cent.
Volatile Matter . . .	31·47 ,, ,,
Fixed Carbon . . .	36·93 ,, ,,
Ash	24·30 ,, ,,

Yield of Oil, 37 gals. per ton.



(Facing page 122).

FIG. 17.—PUR

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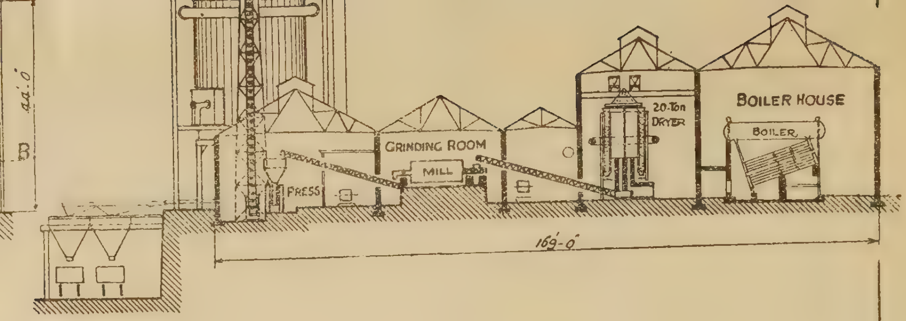

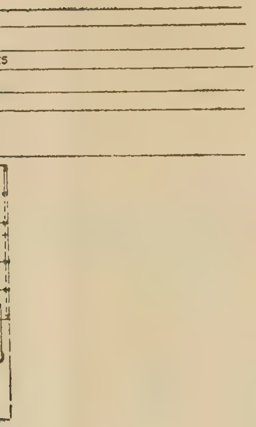

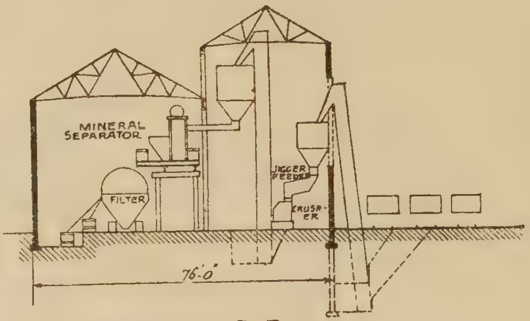

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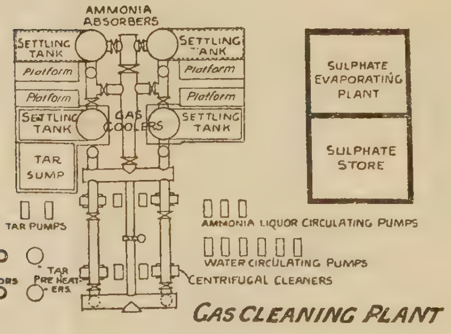

GAS CLEANING PLANT

TTING AND RETORTING PLANT

RBONIZING 1000 TONS per 24 hrs.

SCALE: 16 FEET = 1 INCH.

PROCESS.

Approximate Yield of Oil after Fractionation.

Motor Spirit	1·0 gal. per ton.
Fuel Oil	6·3 ,, ,, ,,
Heavy Oil	16·9 ,, ,, ,,
Wax	3·0 lb. ,, ,,
Pitch	124 ,, ,, ,,

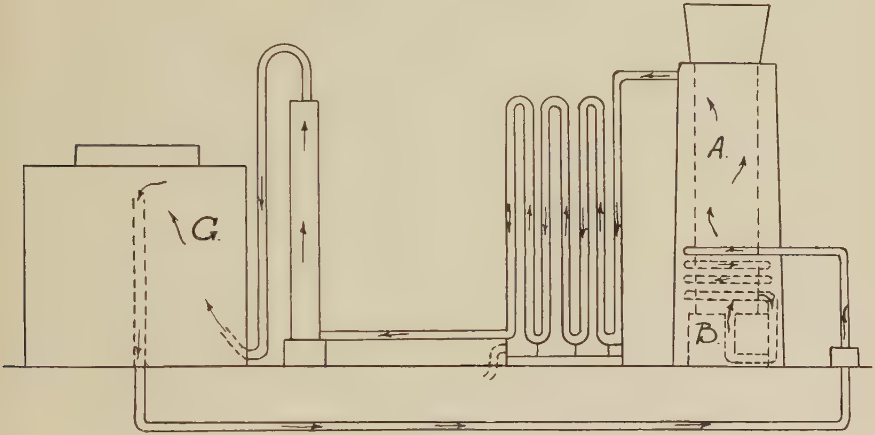

FIG. 18.—DEL MONTE PROCESS.
A—Retort. B—Producer. G—Gasholder.

Newfoundland Shale.

Moisture	1·54 per cent
Volatile Matter	22·35 ,, ,,
Fixed Carbon	2·92 ,, ,,
Mineral Matter	70·65 ,, ,,
Nitrogen	0·24 ,, ,,
Sulphur	2·30 ,, ,,

On distillation, 26 gallons of crude oil (sp. gr. 0·920) were obtained per ton of shale, whilst subsequent fractionation gave the following results:—

Water	0·05 per cent.	
Oil to 150° C.	1·20 ,, ,,	Sp. Gr. 0·796
Oil to 250° C.	16·50 ,, ,,	0·840
Oil to 360° C.	62·20 ,, ,,	0·902
Residue	13·00 ,, ,,	
Loss	7·05 ,, ,,	

This system has undergone considerable modification, but at present it appears to have been succeeded by more recent processes, the original Del Monte process not having established itself.

The Tozer Process

The originality of this process lies in a specially designed retort which is shown diagrammatically in Fig. 19. Owing to the low heat conductivity of coal, the retort is constructed to deal with the coal in thin layers, such layers being in the form of an annular slab, the maximum thickness of which is only four inches. By this means it is claimed that the coal can be carbonised in four and a half hours per charge. The retort, which is made of cast iron, is set vertically. Employing only one annulus per retort, the cubic capacity of the retort would be extremely low, but by the use of radial cast iron fins, it is possible to employ two annuli, one disposed concentrically within the other, the centre passage of the retort being used as a passage for the volatile matter evolved from the coal. It is claimed that by the use of such an arrangement of cast iron fins and an inner annulus, the heat is rapidly conducted to the coal placed in the inner annulus, so that although portions of the coal may be 8 or 12 inches from any directly gas-heated surface, no surface is actually more than 2 inches from an actual heating surface. The retort is slightly expanded towards the discharge (bottom) end, in order to allow the coke to be readily discharged, and to overcome the tendency of the coke to stick in the retort. Coals possessing great or even medium swelling properties could not, of course, be treated in this retort.

The retorts were placed in specially designed recuperative settings, and provided with suitable charging and discharging devices.

In the first instance, the system was worked under a considerable vacuum, but this vacuum has been reduced and now approximates to that employed in ordinary gas works practice. The process has been worked by the Tarless Fuel Syndicate. F. M. Perkin (*loc. cit.*) gives the following as typical yields from the process:

Yorkshire Coal.	Analysis.
Moisture	4·95 per cent.
Ash	5·13 ,, ,,
Volatile matter	29·49 ,, ,,
Free carbon	60·43 ,, ,,
Nitrogen	1·40 ,, ,,
Sulphur	3·22 ,, ,,

This coal yielded 18·0 gallons of water-free oil per ton together with 22 lbs. of ammonium sulphate. The oil on fractionation yielded the following results:—

Motor spirit	3·00	gals.	per	ton.
Intermediate oil	2·51	,,	,,	,,
Fuel oil	8·50	,,	,,	,,
Paraffin wax	8·00	lbs.	,,	,,
Pitch	50·00	,,	,,	,,

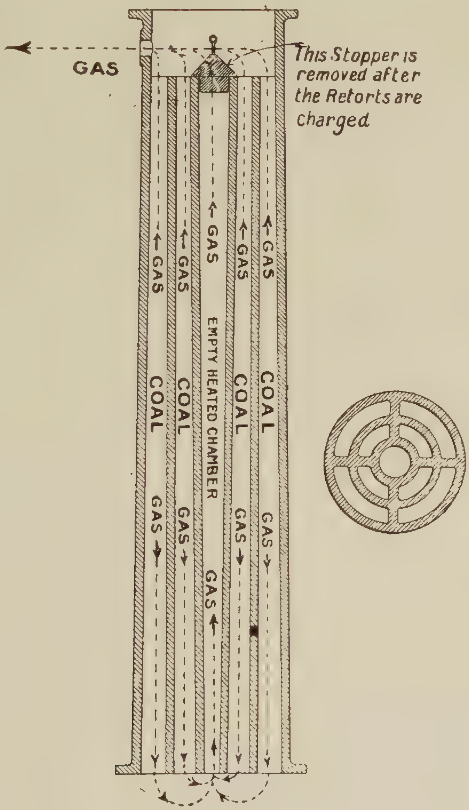

FIG. 19.—TOZER RETORT

The Chiswick Retort

The Chiswick retort is of historical interest, since a battery of thirty of these retorts were installed at the Nottingham Gasworks by the Mineral Oil Production Department, formed in 1917 to undertake the production of oil from indigenous sources.

The retort consisted essentially of an externally heated metallic tube in which a close fitting screw conveyor was caused to rotate, passing the material to be carbonised from a feed hopper through the retort at a predetermined rate, and discharging it through suitable mechanism into a quenching wagon. The retort was placed in a combustion chamber and heated by gas obtained by the process, gas exits being provided equidistant along the top of the retort tube, the gas passing directly to a large foul main, in which the major portion of the tar collected, and then by means of an ascension pipe to by-product plant.

Results obtained with this retort, carbonising cannel coal and kindred substances, are given in " A Treatise on British Mineral Oil " (C. Griffin & Co. Ltd., London, 1919) from which the following are abstracted :—

Results obtained with the Chiswick Retort.

Splint Coals.

Water.	Fixed Carbon.	Ash.	Volatile Matter.	Volatile Matter in Residue.	Crude Oil.	Specific Gravity of Oil.
%	%	%	%	%	Gals. per ton.	
0·7	53·5	20·8	25·7	2·1	30·0	·959
0·3	55·8	18·6	25·6	1·8	40·0	·973
0·5	52·8	19·8	27·4	2·7	20·24	·990
0·5	52·3	20·2	27·5	2·6	30·67	·968

Batts and Jacks.

Water.	Fixed Carbon.	Ash.	Volatile Matter.	Volatile Matter in Residue.	Crude Oil.	Specific Gravity of Oil.
%	%	%	%	%	Gals. per ton.	
2·8	43·1	32·6	24·3	2·6	28·68	·938
2·6	49·0	17·4	33·6	3·6	41·68	·923
0·8	43·6	13·4	43·0	3·5	60·24	·918
2·9	44·2	26·2	29·6	3·8	31·82	·925
1·6	41·0	21·9	37·1	3·0	54·92	·915
			Coals.			
1·8	18·4	61·1	20·5	9·0	6·96	·949
2·5	22·5	47·7	29·8	7·5	19·42	·937
6·1	62·8	5·9	31·3	1·9	20·14	·995
6·6	41·7	20·4	37·9	4·7	41·41	·932

The experience gained with the installation at Nottingham led to the abandonment of this type of retort as a means of producing fuel oil from coal and allied materials.

Fischer and Gluud Retort

Fischer and Gluud* give a description of the plant used in the experimental work which they carried out on the low temperature carbonisation of coal and the resulting products. In such plant they state that they have embodied the conditions essential for success, namely, that the volatile products should not be heated to a temperature higher than that necessary for their volatilisation, and that such volatile products should not be exposed to this temperature for an unnecessarily long period.

The retort is cylindrical, and so mounted that it can be rotated about a horizontal axis. This horizontal axis consists of a hollow shaft, perforated so that the tar and gases can be drawn into the shaft, passing away to suitable tar and ammonia recovery plant, the gas being subsequently utilised to heat the retort.

The retort is surrounded by a well lagged outer cylinder to retain the heat.

This process is of particular interest in so far as it has been used by Fischer and Gluud in their numerous low-temperature carbonisation experiments.

Experimental Plant, The Fuel Research Station, East Greenwich, London

The experimental plant at present in use at the Fuel Research Station, East Greenwich, London, bears a similarity to the Traer and Summers retorts, consisting of a setting of 9 shallow retorts, closed at one end, (each 9 feet long, 2½ feet wide, and 5 inches high) and built into one large combustion chamber 4 feet high. The top and bottom of each retort is slightly arched to give additional strength, and the retorts are heated mainly by the radiant heat of gas in combustion under the arched roof of the combustion chamber, the products of combustion passing through outlets situated beneath the retorts. Each retort is provided with a door which operates valves on the individual gas outlet mains from the retorts, so that when the retort is discharged the main is automatically closed. The gas outlet main from each retort is situated at the closed end of the retort, and the several mains are connected to one large foul main situated at one side of the setting. The coal is placed in specially designed trays which pass into the retorts, the trays being operated by a crane travelling on a runway placed over the retort doors. The coal, after carbonisation, is passed to a cooling hopper, and is in the form of small rectangular cakes owing to the subdivision of the trays by partitions.

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* "Berichte," 1919, 52, 1035-1039.

For a detailed description of this retort, together with the products of the system, the reader is referred to the Report of the Fuel Research Board for the years 1920, 1921 (Second Section : Low Temperature Carbonisation. H.M. Stationery Office).

The Summers Retort

This retort is patented by L. L. Summers, 140 Nassau Street, New York City, N.Y., and an experimental plant is stated to be in course of erection at Hamsburg, Illinois. Operations in England are controlled by Messrs Summers' Carbonising Syndicate, 3 Suffolk Place, London.

The retort consists of a large rectangular chamber 40 feet long, 17 inches wide and 27 inches high, and the coal is passed through the retort by means of a reciprocating iron conveyor, attached to which is an iron plate operated by a ram. The conveyor and plate pass a charge of coal slowly through the retort chamber from a feed hopper, the semi-coke being discharged through a water seal.

The chamber is heated by four gas flues placed horizontally through the side walls of the retort, which is also provided with a suitable heat regenerative system.

It is claimed that either metallurgical or domestic fuel can be prepared by this plant.

The Freeman Multiple Retort

The Freeman Multiple retort consists of a series of shallow carbonising chambers, superimposed one on another, each chamber being maintained at a constant temperature by means of a temperature controlling device, The retort is provided with feed and discharge mechanism, and each separate carbonising chamber contains slowly revolving scrapers, which are designed to expose fresh surfaces of coal and to pass the coal from one chamber to another, through a central communicating duct.

The coal, which must be of small size, is passed in thin layers through succeeding chambers, being submitted to constantly increasing temperatures. Subsequently it is discharged, after passing through a cooling chamber, as a pulverulent product, which must be briquetted if it is to find use as a domestic fuel. Tar oils and ammonium sulphate are the subsidiary products of the system, the gas being used to heat the retort chambers.

The volatile products of the coal are conducted separately from each chamber, and in this manner it is claimed that practically no cracking of tar oils takes place, and much more valuable products are obtained. Fig. 20 shows the general arrangement of the retort.

British Oil and Fuel Conservation Ltd., 5 Hythe Road, Willesden, London, are operating an experimental plant, and in a communication from N. H. Freeman, the patentee, the following results are given:—

Percentage Composition of Coal.

Moisture	1·69
Volatile Matter	25·81
Fixed Carbon	71·10
Ash	1·40
	100·00

Yield Per Ton of Coal Carbonised.

	Percentage.	lbs.
Water	4·26	95·4
Oil	11·78	263·9
Gas	3·94	88·3
Residue	79·60	1782·9
Loss	0·42	9·5
	100·00	2240·0

The oil produced as coming from the condenser was brown in colour and ready for refining. There was produced 27 gallons per ton of coal as received, having an average specific gravity of 0·976. This represents 28·2 gallons per ton of dry coal.

The gas was highly luminous and of a high calorific value. 1,800 c. ft. per ton were produced.

Analysis of Coke

The residue which was in the form of a pulverulent semi-coke, had the following proximate analysis:—

	Percentage.
Volatile Matter	8·35
Fixed Carbon	89·86
Ash	1·79
	100·00

Analysis of Tar Oils

Fractionation of the oil gave the following results:—

Product.	Percentage.	Final Distillation Temperature. °C.	Specific Gravity.	Gallons.
1	5	170	0·719	1·4
2	5	227	0·774	1·4
3	10	258·5	0·867	2·8
4	10	296·0	0·908	2·8
5	10	331·5	0·932	2·8
6	10	363·0	0·926	2·8
7	10	380	0·925	2·8
8	13·7	398	0·934	3·8
Water	1·8	—	—	0·5
Pitch	24·5	—	—	6·9
	100·0			28·0

The 24·5 per cent. of pitch was hard at a temperature of 76° F. It was brittle, blue black in colour and brilliant upon fracture.

The Traer Retort*

The conveyor and plate of the Summers retort are replaced in this retort by iron boxes which pass through the carbonising chamber, being charged with coal at the inlet end, and withdrawn, full of coke, at the outlet end of the retort.

The Fusion Retort

To overcome difficulties associated with the operation of mechanism in a hot retort, the Fusion retort has been designed (Fig. 21).

The special feature of the retort consists in the provision

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* G. W. Traer, "Low Temperature Distillation of Illinois and Indian Coals," Bull. Am. Inst. Min. Eng., 1918, 141, 1463.

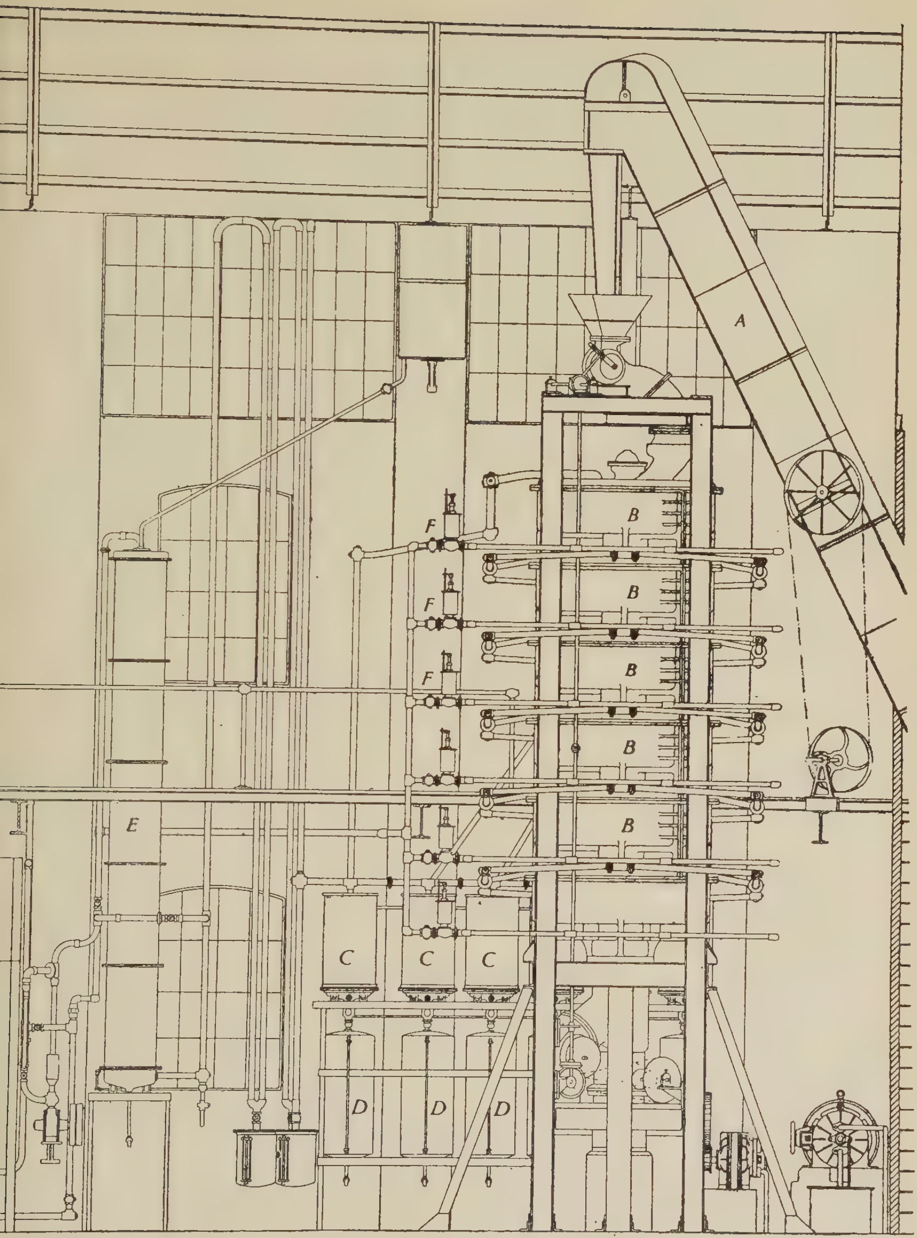

FIG. 20.—FREEMAN MULTIPLE RETORT.

A—Coal feed. B—Chambers of retort. C—Condensers. D—Receiving tanks. E—Scrubber.
F—Temperature control device.

of a "star-shaped breaker" running down the centre of the retort which consists of two rotating shells, concentrically disposed.

The coal, pulverised prior to carbonisation, passes through a mechanical feed down the inner shell, and in a reverse direction down the outer shell, being propelled by rotation of the retort. Fresh surfaces of coal are exposed by the action of the breaker, which is carried a certain distance with the retort, and then falls back on the bed of coal, giving it a glancing or hammer blow, and at the same time freeing the shell from any scale likely to be formed on its inner surface. The retort is heated by means of combustion chambers placed around the outer shell, the gas produced during carbonisation being utilised for such heating.

The coke produced by the retort can be utilised in powdered fuel plant, in gas producers of certain types, and after briquetting for domestic purposes. A five ton experimental plant has been erected at Middlewich where tests have been carried out principally on oil shales.

The Green-Laucks Retort

Experimental plant, of the Green-Laucks system, is in operation by the Denver Coal By-Products Company, Denver, Colorado.*

Cylindrical retorts, 18 ins. in diameter and 18 ft. high, are provided with screw conveyors to pass the charge through the retort.

The plant is of interest in view of the high vacuum under which the system is worked, being as high as 24 ins. of mercury.

The Turner Retort

The Turner retort (Fig. 22) has been designed particularly for the carbonisation of shale, and possesses several distinctive features.

The retort, consisting of a vertical cylindrical chamber, is provided with a mechanical feed and discharge, the material being admitted into a superimposed container through a valve which automatically releases a quantity of material

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* Coal Age, 1919, 15, 810.

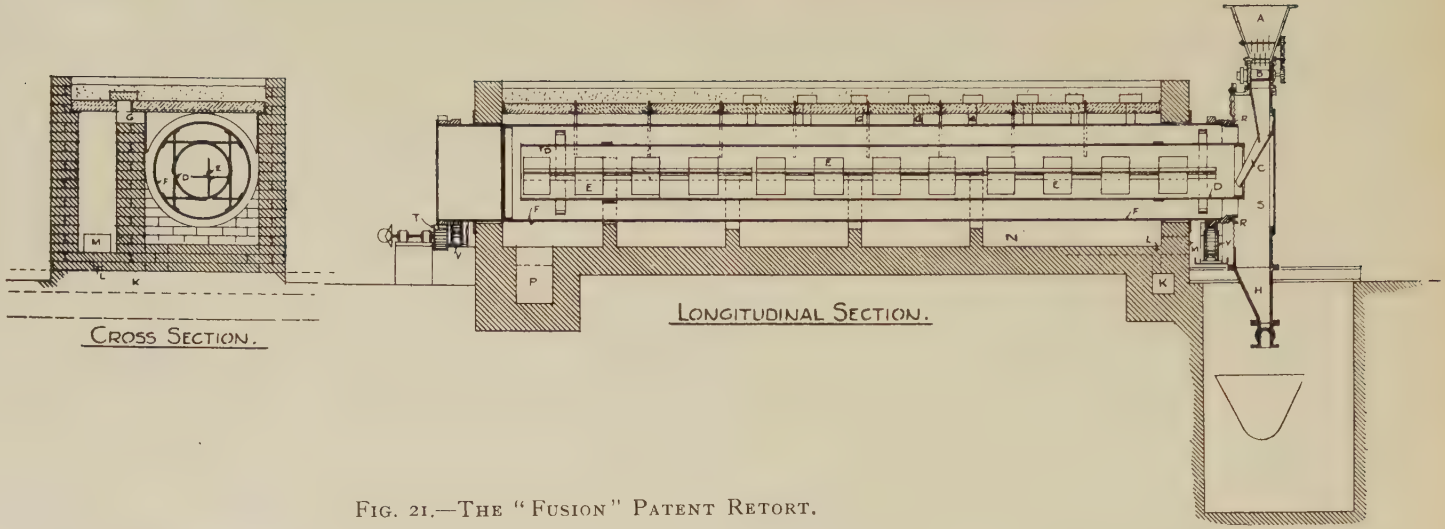

FIG. 21.—THE "FUSION" PATENT RETORT.

A. Raw Material Hopper.
B. Air-tight Feed Valve.
C. Raw Material Guide Pipe
D. Rotating Inner Tube.
E. Breaker or Pulverizer.
F. Rotating Outer Tube.
G. Ports with Dampers for conveying the products of combustion to the furnace round the Rotating Tube F.
H. Spent Material Hopper with Air-tight Valve for discharge.
K. Gas Feed Conduit.
L. Gas Inlet to Combustion Chamber.
M. Air Inlet to Combustion Chamber.
N. Combustion Chamber.
P. Flue to Chimney.
R. Gland for making joint between Feed Chamber and Outer Tube F.
S. Feed Chamber.
T. Gear for Rotating Tube.
V. Rollers upon which the Tube rotates.
W. Oil Vapour and Gas Outlet.

and subsequently grinds itself into a seating, forming a gas-tight fitting. The treated material is discharged by means of a helical screw conveyor, mechanically driven, and placed axially a short distance into the bottom of the retort, the material being passed into a further chamber in which it can be allowed to cool, or in which it can be totally gasified. The retort is internally heated by means of a stream of superheated steam, the volatile products and steam passing out to condensers which are combined with waste heat boilers and feed water heaters. A further feature of the retort, and one which constitutes the main patent in this system is the provision of a valve on the outlet from the retort, so adjusted that when the steam and gases in the retort attain a pressure of five pounds per square inch, the valve opens, and the gases and steam pass out to the condensers, until the pressure is again reduced, whereupon the valve closes.

The material in the retort is thus submitted alternately to a gradually increasing pressure, and a suddenly reduced pressure, whereby it is claimed that the rate of penetration of heat into the mass of material in the retort is increased and subsequently, the sudden evolution of volatile matter from the mass is obtained, resulting in increased output per retort and greater yields per ton of material treated.

The patentee states that this retort has been successfully operated on Bulgarian shales, and plant is at present in course of erection for the Norfolk shale deposits in this country.

The Wallace Retort

This retort consists of a cast iron cylindrical container around which is an annular combustion chamber.

The feature of the retort centres in a perforated tube fixed centrally in the retort, the top of the tube being closed. By this arrangement the gases and tar oils can be recovered without being subjected to higher temperatures than those at which they are evolved from the coal.

A similar principle is involved in the construction of the perforated movable plates of the present Coalite retort.

The Raffloer Retort

According to A. Thau (Coal Age, 1921, 20. 913) no com-

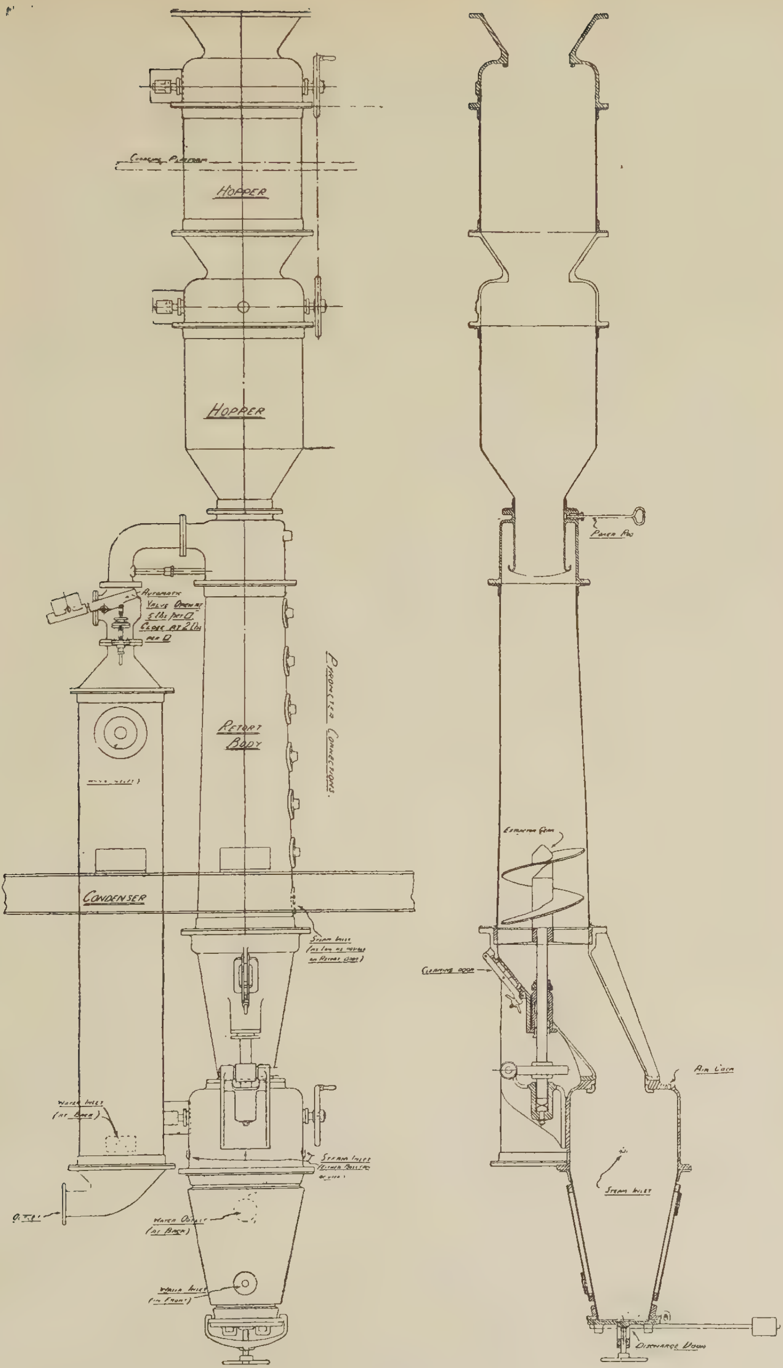

FIG. 22.—TURNER RETORT.

mercial installation of the Raffloer retort had been erected in 1921, the retort being only in the experimental stage. It combines several novel features aiming at the production of a smokeless briquette in a one stage operation. Fig. 23 shows the constructional details of the retort. It consists of a hollow steel shell suitably geared to rotate, and provided on its inner surface with longitudinal fins, so placed as to form containers for the coal charged into the retort, each container tapering towards the discharge end of the retort. The steel shell is fixed between two cast iron plates, so that the feed end of the retort is completely gas tight, the coal being propelled into each individual container in the retort by means of a piston placed directly under the feed hopper, and mechanically driven, whilst the gas and tar oils evolved find exit through the other plate into a chamber from which they pass to by-product plant.

Resting on the bottom of the retort is a cast-iron roller, grooved to gear with the longitudinal fins as the retort revolves, thus completing the container into which the coal is propelled by the piston, and to which reference has already been made.

The retort is heated by means of burners fixed underneath the shell, an annular combustion chamber surrounding the latter, and the products of combustion pass round it to the exit, which is controlled by dampers.

The coal must be pulverised prior to carbonisation, and is then passed to the feed hopper. The retort is revolved in stages, being stationary whilst the piston is propelling coal from the bottom of the feed hopper into one of the containers in the retort which is in line with the piston chamber.

As the containers are tapered towards the discharge end, considerable pressure is brought to bear upon the material in the whole length of the container, and dependent on the stroke of the piston, a bar of material is caused to protrude into the gas exit chamber. As the piston is withdrawn, and the retort commences to rotate until another container registers with the piston chamber, the protruding bar of material is sheared off by a knife working in the exit chamber and the resultant briquette falls into discharging mechanism.

Thau (*loc. cit.*) states that the retort " will have a length

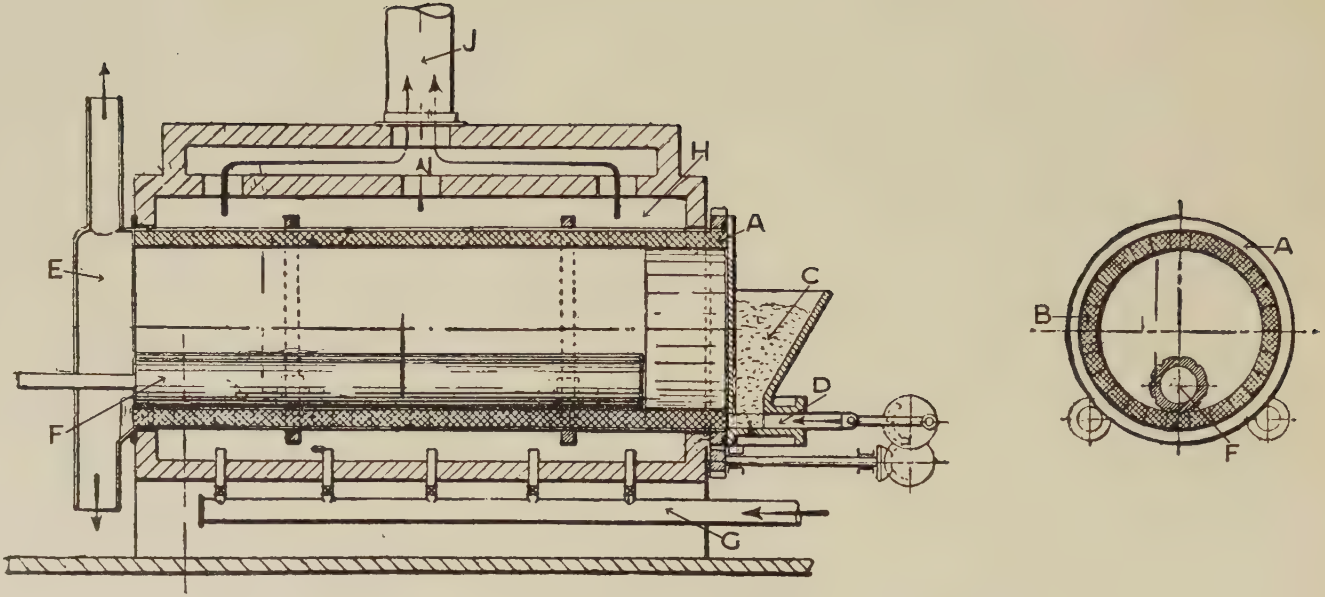

Fig. 23.—Raffloer Retort.

A—Retort shell. B—Containers. C—Feed hopper. D—Piston. E—Gas offtake. F—Grooved roller. G—Burners
H—Combustion chamber. J—Waste gas exit.

of about 35 ft. and a diameter of from 80 to 100 ins." having " a heating surface of approximately 1,076 sq. ft." Allowing one hour for the coal to pass through a container, the capacity of the retort is calculated to be about 50 tons per day.

An average temperature of 842° F. is maintained, whilst it is stated that the tar has a remarkably low free carbon content.

The above retort is interesting as a means of briquetting heated coal whilst in a plastic condition to produce a smokeless briquette, but the construction of the retort would appear to render it liable to frequent breakdown during continued operation.

The Thyssen Retort*

The Thyssen retort (Fig. 24), producing a pulverulent semi-coke, consists essentially of a rotary retort made of steel, and provided with a circular combustion chamber, which entirely surrounds it.

A row of burners placed beneath the retort, inside the combustion chamber, provides the means of heating the retort.

On the inner surface of the retort, spiral ribs are placed to move the material slowly through the retort as it revolves, the coal being fed into the retort by a screw conveyor working at the bottom of a feed hopper, and the gas drawn off under reduced pressure at the discharge end of the retort.

With an overall length of 76 ft. 6 ins., and a height of 5 ft. 9 ins., this retort is stated to have a capacity of 100 tons of coal per day of 24 hours.

The Thomas Retort†

A similar type of retort, but of American design, and known as the Thomas retort, is shown in Fig. 25. This retort is made of steel plate, and is lined with fire-brick. Longitudinally through the fire-brick lining run a number of

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* Stahl und Eisen, 1920, 743.

† Coal Age, 1921, 20, 914.

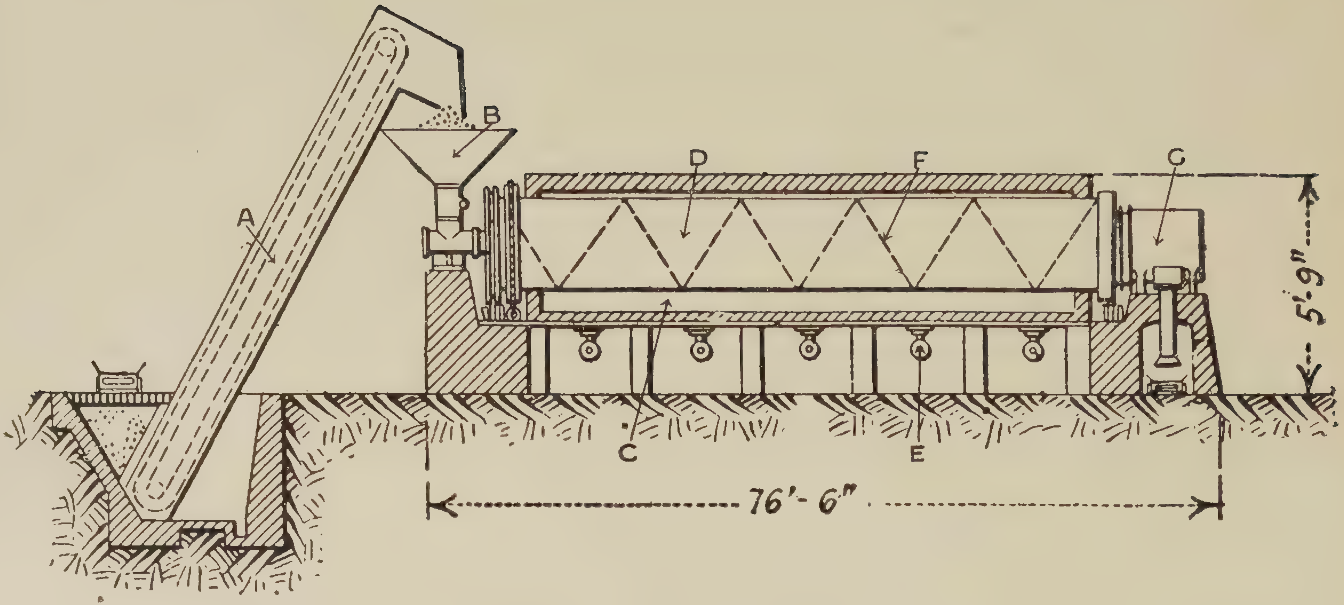

FIG. 24.—THYSSEN RETORT.

A—Elevator. B—Coal hopper. C—Combustion chamber. D—Retort body. E- Burners. F—Spiral rib. G—Discharging chamber.

heating flues, equally spaced around the circumference of the retort. Burners pass through the retort wall into the flues, and the supply of gas to each individual flue is separately governed, an exit being provided for the waste flue gases near the charging end of the retort.

The gases evolved from the coal pass out at the discharging end of the retort through a stationary ascension pipe, the semi-coke being discharged into an air-tight container and finally to a quenching wagon.

Carbonisation is carried out at approximately 500° C.

The Thiery Process

M. Thiery, in a brochure entitled " Four de Distillation par Contact," describes a process in which a series of chambers of from 25 to 100 c. metres capacity are charged and discharged automatically with the material to be carbonised. In starting up, these chambers are charged with incandescent coke, and portions of the subsequently discharged coke, together with a quantity of fresh material, are re-charged into the chambers. The amount of re-charged coke is stated to be dependent on the nature of the material undergoing carbonisation, whilst air-holes are provided in the base of the chambers to admit air, if necessary, to increase the temperature of the mass in the chambers by partial combustion. Apparatus is provided to treat the gas and tar products, and M. Thiery claims that only four men are required to run a plant capable of carbonising 500-600 tons per day.

The Illingworth Process*

A description of the Illingworth process has been reserved to this point since it presents not only a process which has arisen out of purely chemical research, but also since it consists in the conversion of excessively swelling coals into coals from which hard smokeless fuel can be easily made. Apparently the process is one which may be regarded as an alternative to the blending of such coals with a non-caking coal or with coke.

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* English Patent, 161,104. 1921

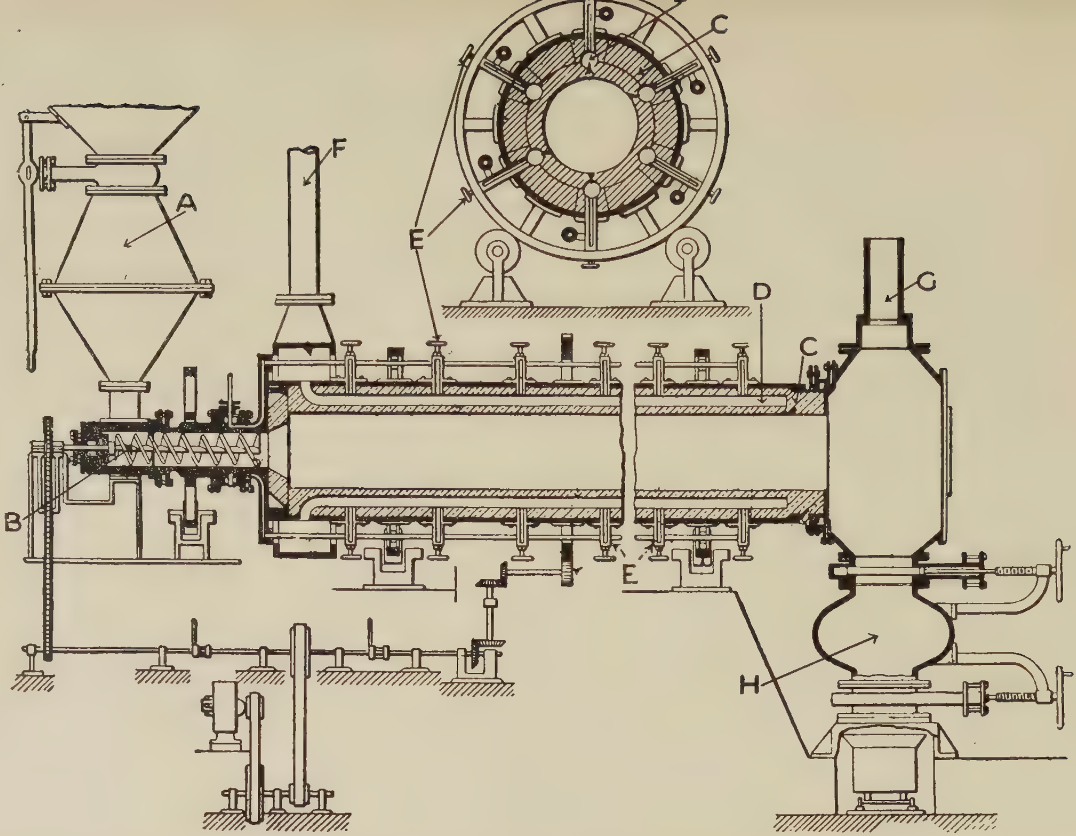

FIG. 25.—THOMAS RETORT.

A—Feed hopper. B—Spiral conveyor feed. C—Firebrick lining. D—Heating flues. E—Burners. F—Waste gas exit. G—Gas offtake. H—Discharging chamber.

Four types of compounds exist in coals, namely:—

(1) The alpha cellulosic compounds.
(2) The gamma or resinic compounds.
(3) The beta cellulosic compounds.
(4) The ulmin compounds.

Illingworth has carried out research work upon these several types of compounds.

Compounds of the alpha cellulosic types do not give coherent coke on carbonisation. They decompose about 500° C., yielding negligible quantities of hydrocarbons, carbon monoxide and hydrogen.

On carbonising coal, the gamma or resinic compounds, melting below their decomposition points, confer plasticity on the mass, and on decomposition serve as the agglutinant or binding agent of the coal. They exist in coal in varying degrees of thermal stability, all being decomposed below 500° C., whilst some are decomposed below 300° C. Their decomposition products are paraffinoid and naphthenic hydrocarbons.

Compounds of the beta type possess no agglutinating power and decompose producing water, phenol and the oxides of carbon. They are present in coals in varying degrees of thermal stability as are the resinic compounds.

The ulmin compounds are highly oxygenated producing the oxides of carbon and water on decomposition. They are present in bituminous coal in negligible quantities.

Illingworth has proceeded to correlate Seyler's classification with the quantitative analysis of all coals upon the basis of these four types of compounds. He states that coals grade from carbonaceous coals, possessing types of beta and gamma compounds which decompose over a short range of temperature, through the bituminous coals possessing types decomposing over a wider range to lignitous coals containing all types of beta and gamma compounds decomposing over the complete range, i.e., up to 500° C.

Carbonaceous coals produce low temperature carbonisation cokes of fair quality, but these coals form only a small percentage of the total bituminous coal available.

By heating bituminous coals over certain ranges of temperature, below the temperature of coke formation and in an inert atmosphere, a selective decomposition of the gamma and beta compounds can be obtained, the less stable compounds being eliminated, and the coals subsequently functioning as carbonaceous coals.

The temperature range can be determined by experiment, and a variety of plant can be employed, provided the fundamental principles are satisfied. The patentee states that the process has been successfully applied in small scale plant at Treforest and that a commercial unit is now in course of erection.

CHAPTER VI

COAL TAR

COMPOSITION OF COAL-TAR—THE CHEMISTRY OF ITS CONSTITUENTS—HYDROCARBONS — OXYGENATED BODIES — SULPHUR BODIES — NITROGEN BODIES—PARAFFINOID AND BENZENOID TARS—TAR YIELDS—TYPES OF TAR—GAS WORKS TAR—COKE OVEN TAR—PRODUCER TAR—BLAST FURNACE TAR—CONCLUSION.

In the foregoing chapters stress has been laid upon the tar produced by the low temperature carbonisation of coal, as of vital importance in the economics of any process designed for such carbonisation, and the opinion has been expressed that probably upon future research on the composition of low temperature tar and its subsequent working up into marketable products, the success or otherwise of a low temperature carbonisation industry will rest.

It has, therefore, been thought necessary to devote considerable space to a description of the work which has already been done upon low temperature tar, prefaced by a description of coal tars in general.

The Composition of Coal Tar

Crude coal tar consists essentially of a heterogeneous mixture of organic compounds, together with a small quantity of entangled ammoniacal liquor. It is with the organic compounds, however, that we are chiefly concerned, although the quantity of "water" present and the ease with which it can be separated, are very important factors governing the value of a tar from the distiller's point of view. The tar distiller, by the process of fractional distillation, divides tar into five or six chief fractions from which, by subsequent treatment, he finally markets about twenty products. The small proportion present of the bulk of coal tar constituents renders their separation, even in the laboratory, an extremely difficult and tedious operation, so much so as to make the process infeasible on a work's scale.

Coal tar, from every source, consists of a number of compounds, varying in actual amounts with each tar, but which can be placed in definite classes, as follows:—

1. *Hydrocarbons*—Bodies containing the elements carbon and hydrogen only. These hydrocarbons can be subdivided into three main types, viz.: Aliphatic, Aromatic and Hydro-aromatic, details of which are given below. A large proportion of bodies of this class is present in every type of coal tar.
2. *Oxygenated Bodies*—Containing carbon, hydrogen and oxygen. This class of substances constitute what are broadly termed " tar acids," and are the source from which phenol or carbolic acid and the cresols (cresylic acid) are derived.
3. *Nitrogen Compounds*—These form a small proportion of all coal tars and contain carbon, hydrogen, and nitrogen. They constitute the " bases " of tar, e.g., pyridine bases. A few of the nitrogenous compounds, however, are not basic in character.
4. *Sulphur Bodies*—Part of the sulphur present in the coal gives rise to sulphur compounds in the tar. They consist, for the most part, of compounds of carbon, hydrogen, and sulphur, and though only present in small quantities, their complete removal from the various coal tar fractions is a difficult and costly process.
5. " *Free* " *Carbon and Pitch*—Although, strictly speaking, free carbon and pitch cannot be classified as belonging to any group of chemical compounds, they are included here for convenience. Free carbon is a black powder obtained by extracting tar or pitch with suitable solvents, e.g., benzene, carbon disulphide, or glacial acetic acid, the free carbon being insoluble. It has been shown that free carbon contains elements other than carbon. Pitch is the residue remaining in the still after the bulk of the oils have been removed. Its composition is very complex, and

its nature is governed to a large extent by the degree to which distillation of the tar is carried out, a soft pitch being formed if some of the oils are left in it, whilst a harder pitch is produced by pushing the distillation to a greater extent.

Hydrocarbons

Aliphatic Hydrocarbons.—Paraffin Series — Saturated (General Formula C_nH_{2n+2}).

These hydrocarbons are termed saturated because the carbon atoms are attached to one another by simple linkings or bonds; derivatives can only be made by the substitution of one or more of the hydrogen atoms by other elements, e.g., chlorine or bromine, and not by the simple addition of such elements. These hydrocarbons are not attacked by such bodies as nitric, sulphuric, or chromic acids in the cold, but are decomposed by these acids on heating.

The first four members of the series, viz., methane, ethane, propane and butane are colourless gases. These are followed by colourless liquids up to C_{15} (namely, pentadecane $C_{15}H_{32}$), the remainder being solids, of a consistency varying from that of vaseline to that of paraffin wax.

Owing to the difference in arrangement of the atoms in the molecule, there are two possible forms of butane (C_4H_{10}), three forms of pentane (C_5H_{12}) and so on. Such bodies, having the same percentage composition, but possessing different properties, are termed isomers or isomeric bodies. This phenomenon of isomerism, as it is termed, is of very frequent occurrence in organic substances, the number of isomers increasing with the molecular weight of the substance, e.g., the hydrocarbon tridecane $C_{13}H_{28}$ has 892 possible isomeric forms, only a few of which, however, are known. For a complete description of isomerism a treatise on organic chemistry should be consulted.

The paraffin hydrocarbons can be prepared synthetically, but occur naturally in large quantities in American petroleum, in natural gas, in ozokerite and in the products of the dry distillation of various carbonaceous materials such as lignites, coals, etc. The following table shows the physical properties of the paraffin hydrocarbons, the " normal " hydrocarbons only being given after hexane, as it is not possible to include all the isomers of the higher members of the series.

The Paraffins

Saturated Hydrocarbons (C_nH_{2n+2})

Formula	Name.		Melting Point. °C.	Boiling Point. °C.		Density.	
CH_4	Methane		−184	−164/760 mm.		0·415 (−164°C.)	
C_2H_6	Ethane		−172·1	−84·1/749 „		0·446 (0°C.)	
C_3H_8	Propane		− 45	−44·5		0·535 (0°C.)	
C_4H_{10}	Butane	Normal	...	+ 1		0·600 (0°C.)	
		Iso	...	−17		0·6029 (0°C.)	
C_5H_{12}	Pentane	Normal	−200	+36·3		0·454 (0°C.)	
		Iso	...	+30·4		0·622	at 20° C.
		Tertiary	−20	+ 9		...	
C_6H_{14}	Hexane	Normal	...	69		0·6603	
		Dimethylisopropyl methane	...	58		0·666	
		Dimethylpropyl methane	...	62		0·6766 (0°C.)	
		Methyldiethyl methane	...	64		0·677	at 20° C.
		Trimethylethyl methane	...	49·6		0·6488	
C_7H_{16}	Heptane		...	98·3		0·683	
C_8H_{18}	Octane		...	125·8		0·702	
C_9H_{20}	Nonane		−51	150		0·718	
$C_{10}H_{22}$	Decane		−31	173		0·7467	
$C_{11}H_{24}$	Undecane		−26	196		0·7581	At Melting Point.
$C_{12}H_{26}$	Dodecane		−12	215		0·7684	
$C_{13}H_{28}$	Tridecane		− 6	234		0·775	
$C_{14}H_{30}$	Tetradecane		+ 4	252		0·775	
$C_{15}H_{32}$	Pentadecane		+10	270		0·776	
$C_{16}H_{34}$	Hexadecane		18	287		0·775	
$C_{17}H_{36}$	Heptadecane		22	303		0·777	
$C_{18}H_{38}$	Octodecane		28	317		0·777	
$C_{19}H_{40}$	Nonodecane		32	330		0·777	
$C_{20}H_{42}$	Eicosane		37	205	At 15 mm. pressure.	0·778	
$C_{21}H_{44}$	Heneicosane		40	215		0·778	
$C_{22}H_{46}$	Docosane		44	224		0·778	
$C_{23}H_{48}$	Tricosane		48	234		0·779	
$C_{24}H_{50}$	Tetracosane		51	243		0·779	
$C_{25}H_{52}$	Pentacosane		53·5	...		...	
$C_{26}H_{54}$	Hexacosane		58	...		...	
$C_{27}H_{56}$	Heptacosane		60	270		0·780	
$C_{28}H_{58}$	Octocosane		60	...		...	
$C_{29}H_{60}$	Nonocosane		63	about 340		...	
$C_{30}H_{62}$							
$C_{31}H_{64}$	Hentriacontane		68	302		0·781	
$C_{32}H_{66}$	Dotricontane (Dicetyl)		70	310		0·781	
....	Members not identified						
$C_{35}H_{72}$	Pentatricontane		75	331		0·782	
....	Members not identified						
$C_{50}H_{102}$	Pentacontane		93	420-422		0·794	
....	Members not identified						
$C_{60}H_{122}$	Hexacontane		101	...		...	

For a description of the individual members of this series the reader is referred to "Coal Tar and Ammonia" (G. Lunge).

Aliphatic Hydrocarbons.—Ethylene Series (Olefines)—Unsaturated (General Formula C_nH_{2n}).

Unlike the preceding class of hydrocarbons the members of this series, owing to the fact that they are "unsaturated" bodies, unite directly with chlorine, bromine or iodine, forming oily liquids. They are also readily soluble in concentrated sulphuric acid and consequently can be removed from a mixture containing olefines and paraffins by agitation with sulphuric acid, the former dissolving in the acid. As in the case of the paraffins, the first members of the series are gases, then follow liquids, and finally solids; furthermore, each member, from butylene upwards, possesses two or more isomeric forms. The higher members of the series readily polymerise and are easily oxidised.

Members of the Series

Formula.	Name.	Melting Point. °C.	Boiling Point. °C.
C_2H_4	Ethylene	−169	−103
C_3H_6	Propylene	...	−48
C_4H_8	Butylene	...	−5
C_4H_8	Pseudobutylene	...	+1
C_4H_8	Isobutylene	...	−6
C_5H_{10}	Amylene	...	+35
C_6H_{12}	Hexylene	...	68
C_7H_{14}	Heptylene	...	98
C_8H_{16}	Octylene	...	124
C_9H_{18}	Nonylene	...	153
$C_{10}H_{20}$	Decylene	...	172
$C_{11}H_{22}$	Endecylene	...	195
$C_{12}H_{24}$	Dodecylene	−31	96 (reduced pressure)
$C_{13}H_{26}$	Tridecylene	...	233
$C_{14}H_{28}$	Tetradecylene	−12	127 (reduced pressure)
$C_{15}H_{30}$	Pentadecylene	...	247
$C_{16}H_{32}$	Hexadecylene (Cetene)	4	274
$C_{18}H_{36}$	Octadecylene	+18	...
$C_{20}H_{40}$	Eicocylene	...	...
$C_{27}H_{54}$	Cerolene	58	...
$C_{30}H_{60}$	Melene	62	...

Higher members have not been identified.

Hydroaromatic Cyclic Hydrocarbons.—Naphthene Series—Saturated (General Formula C_nH_{2n}).

These form a series of saturated hydrocarbons isomeric with the members of the previous series but possessing different properties. They are colourless liquids, with a petroleum-like odour, and are stable when in contact with air. They are acted upon by chlorine and bromine resulting in the formation of substitution products, resembling the paraffins but differing from the olefines in this respect. They are unattacked by strong sulphuric acid in the cold, but are readily sulphonated by fuming sulphuric acid with the formation of sulphonic acids and resins. They occur naturally in many kinds of petroleum oil, especially Caucasian and certain American petroleums. Like the paraffins and olefines, the members of this series possess different isomeric forms, many of which have been identified in petroleum.

The following is a list of a number of the members of this series obtained from different sources:—

Formula.	Name.	Melting Point. °C.	Boiling Point. °C.	Specific Gravity
C_3H_6	Trimethylene	—126	—35/749	...
C_4H_8	Tetramethylene	...	+11-12/726	0·709
C_5H_{10}	Pentamethylene	liquid	50	0·769
,,	Methyltetramethylene	,,	39-42	...
,,	Dimethyltrimethylene	,,	21	...
C_6H_{12}	Hexamethylene (Hexahydrobenzene)	4·5	80·5	0·799
,,	Methylpentamethylene	...	71	0·766
,,	Ethyltetramethylene	...	72·5	...
,,	1 Methyl 2 ethyltrimethylene	...	61·5-62·5	...
,,	1.1.2. Trimethyl Trimethylene	...	57-59/739	...
,,	1.2.3. ,, ,,	...	65-67/755	...
C_7H_{14}	Heptamethylene	—13 to —12	117·5/743	0·830
,,	Methylhexahydrobenzene	...	102-104	0·7964
,,	1.1. Dimethylpentamethylene	...	88·3-88·5	...
,,	1.2. ,, ,,	...	92-93/758	...
,,	1.3. ,, ,,	...	90·5-91	...
,,	1.3. ,, ,,	...	93/743	...
C_8H_{16}	Octomethylene	...	146	856
,,	Dimethylhexamethylene	...	118	781
C_9H_{18}	Nonamethylene	...	...	...
	Higher Naphthenes and their isomeric modifications.			

The members of this series have been identified by many investigators, particularly those working on petroleum, and different authorities give widely differing constants for the same members of the series. This apparently is due to the phenomenon of isomerism.

Aromatic Hydrocarbons.—Benzene Series—Unsaturated (General Formula C_nH_{2n-6}).

The benzenoid hydrocarbons form a very important class of what are known as " aromatic " compounds. They are light, colourless liquids, possessing characteristic odours, and although they belong to the " ring " class of compounds, they are unsaturated, and yield addition, as well as substitution products with the halogens. In the cold, they are not attacked by strong sulphuric acid, but on heating various sulphonic acids are produced. They are readily nitrated, yielding mono-, di- and trinitro-derivatives, and with the exception of benzene, are readily oxidised, the " side " chain being converted into an acid group (COOH) by treatment with permanganate. The hydrocarbons of this series occur chiefly in high temperature tar, but have also been isolated from certain petroleums. The physical properties are given in the following table:—

Formula.	Name.	Melting Point. °C.	Boiling Point. °C.	Specific Gravity.
C_6H_6	Benzene . .	+5	80·4	0·874
$C_6H_5CH_3$	Toluene . .	−93	110	0·869 (16° C.)
$C_6H_4(CH_3)_2$	o-Xylene . .	−28	142	0·893 (0° C.)
,,	m-Xylene . .	−53	139	0·881 (0° C.)
,,	p-Xylene . . .	+13	138	0·880 (0° C.)
$C_6H_5C_2H_5$	Ethylbenzene . .	liquid	138	0·883 (0° C.)
$C_6H_3(CH_2)_3$	Hemellithene (1.2.3. Trimethylbenzene) .	,,	175	...
,,	Pseudocumene (1.2.4. as Trimethylbenzene .	,,	169·5	0·895 (0° C.)
,,	1.3.5. Mesitylene . .	,,	165	0·865 (14° C.)
$C_6H_5C_3H_7$	n-Propylbenzene . .	,,	159	0·867 (14° C.)
,,	iso-Propylbenzene (Cumene)	,,	153	0·866 (16° C.)
$C_6H_2(CH_3)_4$	1.2.3.4. Prehnitene . .	−4	204	...
	1.2.3.5. Isodurene . .	liquid	195	...
	1.2.4.5. Durene . .	+80	192	...
$C_6H(CH_3)_5$	1.2.3.4.5. Pentamethylbenzene . . .	51·5	231	0·847 (104° C.)
$C_6(CH_3)_6$	Hexamethylbenzene .	166	265	...

Other Hydrocarbons

Various other hydrocarbons occur in coal tar, but with a few exceptions, they are only present in very small amounts.

The different series, with the first member of each separate series, are shown below.

Name of Series.	General Formula.	First Member.	Boiling Point. °C.
Acetylene Series .	. C_nH_{2n-2}	Acetylene C_2H_2	Gas
Naphthelenes	. C_nH_{2n-2}	Tetrahydrobenzene C_6H_{10}	83
Dihydro addition products of Benzene Series .	. C_nH_{2n-4}	Dihydrobenzene C_6H_8	84
Naphthalene Series .	. C_nH_{2n-12}	Naphthalene $C_{10}H_8$	M.P. 80
Anthracene Series .	. C_nH_{2n-18}	Anthracene $C_{14}H_{10}$	M.P. 213

The most important of these hydrocarbons are naphthalene and anthracene. Naphthalene is a white solid, crystallising in plates which melt at 79° C., and boiling at 218° C. It is extremely volatile even far below its boiling point. It is largely used in the manufacture of intermediates for dyestuffs. Anthracene resembles naphthalene in appearance and general properties, but melts at a much higher temperature, viz., 213° C., and boils at 351° C.

Oxygenated Bodies—Tar Acids—Phenols

Owing to the fact that these bodies may constitute as much as 50 per cent. of low temperature tar, they are of paramount importance. Constitutionally, they are hydroxy-derivatives of the benzene hydrocarbons, in which one or more of the hydrogen atoms of the hydrocarbon are replaced by hydroxyl or —OH groups, e.g., benzene C_6H_6, yields phenol C_6H_5OH; resorcinol $C_6H_4(OH)_2$, etc. The phenols are classified according to the number of hydroxyl groups they contain; if one such group is present, as in ordinary phenol, it is said to be a monohydric phenol, whilst phenols containing two or three hydroxyl groups are termed dihydric and trihydric phenols respectively. The phenols are soluble in alcohol and ether, whilst many of them, especially di- and trihydric phenols, dissolve in water. They are readily soluble in a solution of caustic soda, the solutions yielding, on evaporation, solid crystalline bodies termed phenates. By this means they can be readily separated from the hydrocarbons associated with them in coal tar, whilst, upon acidifying, even with carbon dioxide, the phenates are decomposed re-generating the phenols. Most of the phenols, when pure, are crystalline solids, possessing characteristic odours.

They are poisonous and also possess antiseptic properties rendering them extremely valuable as disinfectants. The phenols are readily attacked by nitric acid and by the halogens. Although they can be prepared synthetically, many of them are also obtained from natural sources, e.g., by the distillation of wood and coal; and in the case of the di- and trihydric phenols, from resins and tannins by fusion with caustic potash. Care must be taken to differentiate between the word " phenol " as representing carbolic acid, and the word " phenols " as a general term for all the members of the series.

Monohydroxy Phenols

Formula.	Name.	Melting Point. C.	Boiling Point. °C.	Specific Gravity.
C_6H_5OH	Phenol	42·5	183	1·039 (58·5° C.)
$CH_3C_6H_4OH$	o-Cresol	30	191	1·043 (23° C.)
,,	m-Cresol	4	203	1·035 (13·6° C.)
,,	p-Cresol	36	202	1·034 (18° C.)
$(CH_3)_2C_6H_3OH$	o-Xylenol 1.2. dimethyl 3 hydroxyphenol	73	213	...
,,	o-Xylenol 1.2. dimethyl 4 hydroxyphenol	65	222	...
,,	m-Xylenol 1.3. dimethyl 2 hydroxyphenol	49	...	...
,,	m-Xylenol 1.3. dimethyl 4 hydroxyphenol	25	209	1·036 (0° C.)
,,	m-Xylenol 1.3. dimethyl 5 hydroxyphenol	63	218	...
,,	p-Xylenol 1.4. dimethyl 2 hydroxyphenol	75	209	0·971 (81°. C.)
$C_2H_5C_6H_4OH$	o-Ethylphenol	liquid	203	1·037 (0° C.)
,,	m-Ethylphenol	−4	214	1·040 (0° C.)
,,	p-Ethylphenol	+45	219	...
$(CH_3)_3C_6H_2OH$	Mesitol 1.3 5. trimethyl 2 hydroxyphenol	71	219·5	...
	Pseudocuminol 1.2.4. trimethyl 5 hydroxyphenol	73	235	...
	Hemimellithenol 1.2.3. trimethyl 5 Hydroxyphenol	81	...	...
$(CH_3)_4C_6HOH$	Prehnitenol 1.2.3.4. tetramethyl 4 Hydroxyphenol	87	266	...
	Durenol 1.2.4.5 . tetramethyl 3 Hydroxyphenol	117	250	...
$(CH_3)_5C_6OH$	Pentamethylphenol	125	267	...

Polyhydroxy Phenols

Formula.	Name.	Melting Point. °C.	Melting Point. °C.	Specific Gravity.
$C_6H_4(OH)_2$	Catechol 1.2	104	...	...
	Resorcinol 1.3	110	270	...
	Hydroquinone 1.4	169	...	...
$C_6H_3(OH)_3$	Pyrogallol 1.2.3	132	210	...
	Trihydroxybenzene 1.3.4	140·5	...	...
	Phloroglucinol	...	...	...
$C_6H_2(OH)_4$	Tetrahydroxybenzene 1.2.4.5	...	220	...

Owing to the importance of tar acids in low temperature tar, a short account of a few of the individual members of the series is given.

Phenol (Carbolic Acid) (C_6H_5OH)

When pure, this is a white solid, crystallising in needle-shaped crystals, but readily turning a reddish colour on exposure to air. Phenol is a powerful poison and attacks the skin. It is used largely in the preparation of disinfectants for various purposes, and is also employed as the base for the synthesis of nitrophenols, picric acid, salicylic acid, phenacetin and other organic substances. It is not very soluble in water, but readily dissolves in caustic soda, yielding sodium phenate. The principal source of phenol is ordinary coal tar, but during the war it was also manufactured synthetically from benzene, by sulphonating the latter and subsequently converting the sulphonic group into the hydroxy group.

Cresols—Cresylic Acid ($C_6H_4(CH_3)OH$)

The three cresols together form what is commercially known as cresylic acid. This is a light brown coloured liquid, boiling between 185° C. and 206° C., and possessing a specific gravity of 1·038-1·044. It has a strong phenolic odour, is less poisonous than ordinary phenol, and possesses more pronounced antiseptic properties. It is only sparingly soluble in water but is miscible in all proportions with benzene, ether, alcohol, petroleum ether, and glycerine. It is principally derived from the distillation of coal tar.

The three bodies composing cresylic acid are ortho-, meta-, and para-cresol. When pure, o-cresol and p-cresol are solids at the ordinary temperature, but when impure may be liquids, whilst m-cresol is always liquid at ordinary temperatures.

Xylenols $C_6H_3(CH_3)_2OH$
There are six isomeric members of this group, and though present in coal tar they are rarely separately isolated from it, being obtained as a light brown liquid containing smaller amounts of other tar acids. Like the cresols, they possess strong antiseptic properties.

Sulphur Bodies

All tars contain a small proportion of sulphur compounds. These may be divided into two classes: (1) inorganic sulphur compounds, such as sulphuretted hydrogen and ammonium sulphide, and (2) organic sulphur compounds, such as carbon bisulphide and thiophene.

Though present to only a small extent, the removal of the last trace of sulphur from the various tar fractions is an extremely difficult and costly process. The following table indicates the physical properties of the principal sulphur compounds occurring in coal tar:—

Formula.	Name.	Melting Point. °C.	Boiling Point. °C.
H_2S	Sulphuretted hydrogen	...	...
$(NH_4)_2S$	Ammonium sulphide	...	...
$(NH_4)CNS$	,, sulphocyanide	...	...
SO_2	Sulphur dioxide	...	...
CS_2	Carbon disulphide	Liquid	47
	Mercaptans	...	...
C_4H_4S	Thiophene	Liquid	84
C_5H_6S	α Thiotolene	,,	113
,,	β ,,	,,	113
C_6H_6S	$\alpha\alpha$ Thioxene	,,	135-136
,,	$\alpha\beta$,,	,,	136-137
,,	$\alpha\beta'$,,	,,	137-138
,,	$\beta\beta$,,	,,	136-137
	Higher Thiohydrocarbons		

Nitrogen Bodies

These substances can be divided into basic and non-basic bodies.

The principal basic bodies are members of one of three series, viz., aniline and its homologues, pyridine and its homologues, and the quinoline series.

Aniline and the toluidines are colourless liquids with characteristic odours and are lighter than water. They rapidly turn yellow and then reddish-brown upon standing. They are readily dissolved by acids, e.g., hydrochloric or sulphuric acids, forming the corresponding salts, this property affording a means of separating them from the hydrocarbons.

Pyridine and its homologues are colourless, evil-smelling liquids, very stable to oxidising agents, being unaffected by fuming nitric and by chromic acids, but dissolving in hydrochloric and sulphuric acids to form salts. Unlike the previous series, pyridine and its homologues are fairly soluble in water, and their specific gravities are less than unity.

The members of the quinoline series are liquids (with the exception of isoquinoline) of high boiling point, possessing basic properties and not unpleasant odours.

Of the non-basic nitrogenous bodies occurring in coal tar, the principal ones are—acetonitrile, a liquid of low boiling point, miscible with water and possessing a not unpleasant odour; pyrrol, a colourless liquid readily turning brown in the air, almost insoluble in water or alkalies but readily soluble in ether and alcohol, unacted upon by most of the ordinary chemical reagents; and carbazol and its derivatives, solids of high melting points and very high boiling points. From ordinary coal tar, carbazol separates out with the crude anthracene.

The table below gives the physical properties of the chief nitrogenous bodies.

Formula.	Name.	Melting Point. °C.	Boiling Point. °C.	Specific Gravity.
NH_3	Ammonia	...	...	...
$C_6H_5NH_2$	Aniline	—8	182	1·020 (16° C.)
$CH_3C_6H_4HN_2$	o-Toluene	...	...	...
,,	m- ,,	...	...	...
,,	p- ,,	...	...	...
C_5H_5N	Pyridine	...	116·7	0·9858 (0° C.)
C_6H_7N	α Picoline	...	135	0·9613 (0° C.)
,,	β ,,	...	138	...
,,	γ ,,	...		...
C_7H_9N	αα Lutidine	...	143	...
,,	αβ ,,	...	162-163	...
,,	αγ ,,	...	157	...
,,	αβ1 ,,	...		...
,,	βγ1 ,,	...	163·5-164·5	...
,,	ββ' ,,	...	169-170	...
,,	γ Ethylpyridine	...	164-166	...

Formula.	Name.	Melting Point. °C.	Boiling Point. °C.	Specific Gravity.
$C_8H_{11}N$	α' γ Collidine	...	171-172	...
,,	α' βγ ,,	...	165-168	...
	Higher pyridine homologues			
C_9H_7N	Quinoline	...	239	1·081
,,	Iso-quinoline	28	236	...
$C_{10}H_9N$	α Methylquinoline	liquid	243	1·072 (15° C.)
$C_{13}H_9N$	Acridine (non basic)	107	above 360	...
CH_3CN	Acetonitrile	liquid	79	0·835
C_4H_5N	Pyrrol	,,	133	1·077
$C_{12}H_9N$	Carbazol	238	355	...

Paraffinoid and Benzenoid Tars

The composition of a tar is dependent upon the nature of the coal carbonised, the temperature gradient at which the coal is heated, the rate of removal of the crude gas from the heated zone, and the temperature to which the tar is subjected, subsequent to evolution from the coal mass. The temperature gradient, and the subsequent temperature to which the tar is subjected depend upon the system of carbonisation and type of retort employed, and the mass of coal heated in the retort.

Tars produced in the initial stages of the decomposition of coal are of a " paraffinoid " nature, i.e., the paraffin type of hydrocarbons predominate as distinct from the benzenoid type of hydrocarbons.

Low temperature tars are characteristic " paraffinoid " tars.

As the temperature increases, and carbonisation proceeds, secondary reactions begin to take place with the decomposition of certain bodies in the tar, resulting in the formation of aromatic hydrocarbons of the benzenoid type. At the same time, conversion of other types of compounds is taking place, and with a continued rise in temperature a tar is obtained which is characterised as a high-temperature tar.

In the case of a true high temperature tar, all secondary reactions have been completed, and the tar has become a " benzenoid tar."

Between a true low temperature and a true high temperature tar, tars of a composition midway in type between paraffinoid and benzenoid tars are produced, such tars being formed in what may be termed a transition period between 550° C. and 750° C.

Horizontal gas retort tar is a typical benzenoid tar.

Tar Yields per ton of Coal Carbonised

The yield of tar obtainable from any coal depends primarily upon the constitution of the coal. Numerous experimenters have endeavoured to correlate coal constitution with the yield of tar. Bunte, working on German coals, correlated the yield of tar obtained by carbonising the coal under normal gas works conditions, with the oxygen content of the coal as follows:—

Oxygen Content of Coal on Ash and Moisture-free Basis.	Kilos. of Tar per 100 kilos. of Coal Carbonised.
13·04	5·22
11·64	5·79
10·13	5·33
8·27	4·09

A maximum yield of tar was obtained using a coal containing 11·64 per cent. of oxygen, and above this amount the yield of tar diminished, whilst carbonising a coal of a cannel nature containing 7·27 per cent. of hydrogen, 8·81 kilos of tar per 100 kilos of coal carbonised were obtained, the coal having an oxygen content of 10·78 per cent. on a moisture and ash-free basis. Lewes states that if a coal contains 10 to 11 per cent. of oxygen and possesses a hydrogen content well above 5 per cent., the tar distillates will be high and rich in heavy hydrocarbons.

If bituminous coals are carbonised at various temperatures, the quantity of tar obtained reaches a maximum and then falls rapidly with a continued rise in the temperature of carbonisation. The following average figures may be taken to show this, but it must be clearly understood that different results may be obtained according to the type of coal employed.

Temperature of Distillation. °C.	Gals. of Tar obtained per ton of Coal Carbonised.
300	—
400	24
500	21
600	18
700	15
800	12
900	10

As the temperature rises, there is a corresponding increase in the specific gravity of the tar, low temperature tar being much lighter than that obtained at high temperatures.

Under ordinary conditions of working, using the coal most suitable for their respective processes, the amount of tar obtained per ton of coal may be taken on the average as follows:—

Source of Tar.	Approximate Yield. Gals. of Tar per Ton of Coal treated.
Horizontal retort	10
Vertical gas retort	10-12
Coke oven	9
Producer gas plant	8-9
Blast furnace	7
Low temperature carbonisation processes	18-25

Gas works, coke ovens, blast furnaces and producer plants are the sources of production of practically the whole of our supplies of coal tar.

Gas Works Tar

This tar is derived from the carbonisation of coal carried out with the primary object of obtaining gas for heating and illuminating purposes, with the result that a high yield of gaseous products is obtained at the expense of the coke and tar. Carbonisation is carried out in three types of retorts:—

1. Horizontal.
2. Inclined.
3. Vertical.

On the Continent, large chamber ovens, designed to perform the work of both gas retort and coke oven, have come into use at several of the large gas works, but have not yet found favour in this country.

The varying conditions in the three types of gas retorts result in the production of three different kinds of tar, even when using the same type of coal in each retort. Owing to the position and shape of the horizontal retort and to the method of heating it, the coal is subjected rapidly to a high temperature and the vapours evolved before passing out of the retort, come in contact with the hot sides of the retort and are partially " cracked " or decomposed. When small charges were employed in the retort, this "cracking" took place to a very marked degree, yielding a heavy, viscous tar containing a large amount of pitch and free carbon, but with the advent of fully charged retorts, the tars from horizontal and inclined retorts have improved in this respect.

Horizontal retort tar possesses a higher specific gravity than any of the other varieties of tar, varying from 1·15 to 1·25. It is truly benzenoid in character, the light oils obtained being practically devoid of any paraffins, whilst the naphthalene and anthracene content is much higher than in vertical retort tar.

In the continuous vertical retort, e.g., the Glover-West retort, the coal is fed continuously into a heated vertical chamber, passes through, and is withdrawn at the bottom. Owing to the mass of coal in the retort, and to the method of heating, the coal is only heated up gradually and the vapours evolved pass out of the retort before very marked "cracking" has taken place.

Vertical retort tar is much less viscous, contains less free carbon and pitch than horizontal retort tar, and also possesses a lower specific gravity, 1·05 to 1·18. Its light oil content is higher, but appreciable quantities of paraffins occur in the tar, being found in the light oils to a marked degree. The tar obtained from intermittent vertical and from inclined retorts is intermediate in composition between horizontal and continuous vertical retort tar. Sharples, in a paper read before the North British Association of Gas Managers, September 7th, 1917 (Gas J. 1917. 139. 469) gives the following figures showing the results obtained by carbonising the same class of coal at two different works in Scotland.

	Percentage Composition of Tars.			
	Horizontal Retorts.		Vertical Retorts.	
Water	1·55		2·42	
Crude Naphtha	2·62	12·06	2·44	18·55
Light Oil	9·44		16·11	
Carbolic Oil	12·09		14·10	
Creosote Oil	13·00		21·47	
Pitch	61·30		43·38	
Loss	—		0·08	
Specific Gravity of the Tar at 60° F.	1·20		1·075	

Upon rectifying the various fractions, the following results were obtained:

	Horizontal.			Vertical.		
	Gals. per Ton of Coal Carbonised.	Percentage by Weight of Coal.	Lbs. per Ton of Coal.	Gals. per Ton of Coal Carbonised.	Percentage by Weight of Coal.	Lbs. per Ton of Coal.
90's Benzol	2·507	0·984	1·299	1·340	0·515	0·747
90's Toluol	0·818	0·318	0·420	0·832	0·317	0·460
Solvent Naphtha	2·537	0·986	1·302	4·252	1·615	2·342
Total	5·862	2·288	3·021	6·424	2·447	3·549
Heavy Naphtha	3·979	1·652	2·178	6·240	2·409	3·493
Refined Pyridine	0·160	0·076	0·100	0·354	0·160	0·232
Heavy Pyridine Bases	1·165	0·532	0·702	0·832	0·383	0·555
60's Carbolic Acid	0·200	0·094	0·124	2·311	1·074	1·557
Cresylic Acid	5·230	2·451	3·234	12·480	5·913	8·574
Light Creosote	43·065	20·381	26·902	16·039	7·126	10·339
Heavy Creosote				66·102	31·009	44·965
Naphthalene	9·00	4·620	6·098	6·839	3·455	5·017
Pitch	...	66·425	87·700	...	43·380	62·901
NH_3 Liquor 3·3% NH_3	2·980	1·356	1·800	5·366	2·420	2·030
Loss	0·280	0·125	0·165	0·322	0·224	0·325

Composition of the Naphthas.	Percentage Paraffins.	Specific Gravity.	Percentage Paraffins.	Specific Gravity.
90's Benzol	below 1 per cent.	0·881	19	0·865
90's Toluol		0·872	12	0·863
Solvent Naphtha		0·871	6	0·851

Coke Oven Tar

This is a product obtained from the carbonisation of coal in large horizontal ovens, the coke produced being used for metallurgical purposes. Owing to the high temperature employed, the nature and mass of the coal, together with the long period of heating, the yield of tar per ton of coal is usually lower than in the case of gas manufacture. In nature, the tar somewhat resembles lightly charged horizontal retort tar, but is slightly thinner, and contains less pitch and free carbon. The quantity of paraffins in the tar is usually low, but varies somewhat with the type of oven and the size of the charge, the type of oven apparently being a very important factor governing the composition of the resulting tar. Prevost Hubbard (Coke Oven Tars of the United States, Circular 97, Office of Public Roads, U.S. Dept. of Agriculture) gives analyses of tars from 26 different coke ovens, and found the specific gravity to range from 1·133 to 1·214, and the free carbon content to vary from 2·73 per cent. to 16·80 per cent. with an average of 8·38 per cent.

Schmitz (Die Flüssige Brennstoffe, Berlin, 1919, 59) gives the following analyses of coke oven tars from various sources :—

	1	2	3	4	5	6	7	8
Specific Gravity .	1·16	1·145-1·191	1·17	1·1198	...	...	...	...
Water . . .	2·0	2·69	2·3	trace	6·60	3·20	3·40	3·70
Light Oil . .	1·5	1·38	3·7	6·5	2·30	0·80	4·10	3·20
Middle Oil . .	7·0	3·46	9·8	10·5	10·20	5·00	10·70	10·50
Heavy Oil . .	14·0	9·93	12·0	7·6	8·0	8·40	8·60	7·40
Anthracene Oil .	14·0	24·76	4·3	44·3	26·70	22·70	19·00	16·80
Pitch . . .	60·0	56·44	67·0	30·5	45·19	58·60	55·40	57·20
Loss . . .	1·5	1·34	0·9	0·4	0·28	1·30	1·60	0·20

Producer Tar

A considerable quantity of tar is recovered from Mond gas and other types of producer plant. The tars produced vary considerably in composition and consistency, some being thin and watery whilst others are almost solid. As a rule, they are somewhat difficult to work owing to the fact that the water present is often excessive, and, furthermore, it generally forms an emulsion with the tar, failing to separate even on standing for a long period. One peculiar feature about this class of tar is that they rarely contain any naphthalene, whilst the quantity of oils boiling even below 230° C. is extremely low.

Blast Furnace Tar

There occur in certain coalfields, e.g., in the West of Scotland, coals which do not flame, or swell during heating and yet produce a firm coke. These " splint " coals, as they are termed, can be used directly in a blast furnace and yield a tar totally different from any of the preceding varieties. The tar is very thin, its specific gravity being usually less than unity, and owing to the high oxygen content of the coal, the tar contains a higher percentage of tar acids—hence the name " phenoloid tar." The pitch content is low, but although it is bright and hard, it contains a high percentage (5-30 per cent.) of ash and 15-25 per cent. of free carbon.

Watson Smith (J.Soc.Chem.Ind. 1883. 2. 495; J.Chem. Soc. 1886. 49. 17) gives the following as a typical analysis of blast furnace tar:—

Specific Gravity . . . . 0·954

	Percentage by Volume.	Percentage by Weight.	Specific Gravity.
Below 230° C. Water	30·60	32·3	1·007
Below 230° C. Oil	2·91	2·8	·899
230-300° C.	6·97	7·1	·971
300° C. until oils solidify	13·02	13·5	·994
Oils solidifying on cooling (soft paraffin scale)	16·75	17·3	·987
Coke	—	21·5	—
Loss	—	5·5	—

On standing a few days, all the fractions darkened considerably in colour, a property common to the distillates from many low temperature tars. Naphthalene was present only in small quantity, while anthracene was absent. The light oils only contained very small amounts of benzene and its homologues.

Hooper (J.Soc.Chem.Ind. 1910. 29. 1438) gives the following figures for the composition of blast furnace tar:—

Specific Gravity	0·954
Distillate to 230° C.	2·9%
,, ,, 300° C.	6·97%
,, ,, 350° C.	33·0%
Pitch	55-60%

The following table, due to Constam and Schläpfer (Zeits. des Vereines deut. Ingenieure, Oct. 1913) will serve to indicate the range in composition of tars from various sources:—

Nature of Tar.	Horizontal Retort.	Inclined Retort.	Dessau.	Woodall-Duckham.	Large Carbonising Chamber.	Coke Oven.
Specific Gravity at 15° C.	1·156-1·235	1·125-1·157	1·057-1·123	1·081-1·101	1·064-1·089	1·140 1·182
Flash Point (Closed) °C.	67-92	52-78	49-75	41-52	35-71	90-135
Flash Point (Open) °C.	93-129	79-107	70-102	71-90	70-93	108-166
Self-Ignition Temperature in Platinum Crucible in a Current of Oxygen, °C.	520-630	490-520	510-530	500-510	480-510	about 600
Fractionation Percentage by vol. of tar exclusive of water and ash						
Light Oil . 0-170° C.	1·0-6·6	1·5-6·7	1·0-9·3	3·0-8·4	2·5-10·0	0·0-0·0*
Middle Oil . 170-230° C.	10·2-14·0	14·7-17·8	16·0-24·0	13·0-16·9	21·0-24·0	1·0-17·0
Heavy Oil . 230-270° C.	8·5-13·0	4·9-14·4	8·8-18·0	11·2-13·0	9·5-12·5	6·5-14·0
Anthracene Oil 270-350° C.	9·9-21·9	12·9-21·0	19·2-24·5	19·5-21·0	17·5-24·0	19·0-27·5
Pitch .	51·7-66·5	47·6-54·7	31·5-47·0	44·0-51·0	39·0-41·5	50·0-65·0
Percentage Coke from Pitch	32-47	32-40	16-27	20-25	21-22	16-34
Composition of Crude Tar						
Water, per cent	0·00-8·72	1·11-7·30	0·77-3·63	1·11-2·84	1·29-5·82	0·59-6·67
Ash, per cent	0·00-0·06	0·01-0·07	0·00-0·00	0·00-0·03	0·00-0·00	0·04-0·36
Cal. Val. of dehyd. Tar, net B.Th.U's. per lb.	15,745 —15,887	15,790 —15,952	15,898 —16,335	15,912 —16,020	15,826 —16,025	15,793 —16,049
Composition of dehydrated ash-free Tar						
Carbon, per cent.	90·4-92·9	89·3-90·4	87·6-89·9	87·9-88·8	89·1-89·3	89·6-92·2
Hydrogen, per cent.	4·7-5·5	5·9-6·4	6·0-7·3	6·6-7·2	6·7-7·1	5·1-5·7
Oxygen and Nitrogen, per cent	1·7-3·2	3·2-3·9	2·6-4·9	4·1-4·7	3·6-5·2	2·2-4·0
Sulphur, per cent	0·5-1·0	0·4-0·7	0·4-0·6	0·5-0·9	0·3-0·6	0·4-1·2
Yield of Coke, per cent	15·1-33·3	15·3-21·7	4·0-10·8	7·0-9·7	7·1-7·3	7·6-16·9
Free Carbon, per cent	9·3-27·6	10·0-19·3	1·1-5·7	3·1-5·7	2·3-3·0	2·2-10·3
Naphthalene, per cent	4·1-6·0	1·2-3·3	0·2-2·5	0·1-1·0	0·6-2·1	0·5-9·8
No. of Samples examined	9	8	11	4	4	12

* Light oils removed in benzol washing.

CHAPTER VII

LOW TEMPERATURE TAR

COMPOSITION—VACUUM TAR—WORK OF JONES AND WHEELER—PICTET—LOW TEMPERATURE TAR PROPER—CONSTITUENTS—HYDROCARBONS—RESEARCH ON HYDROCARBONS—PARR AND OLIN—CHURCH—FULKS—WHITAKER AND CROWELL—FISCHER AND GLUUD—MORGAN AND SOULE—OXYGENATED BODIES (A) TAR ACIDS—RESEARCH ON TAR ACIDS—JONES AND WHEELER—PICTET—FISCHER—MORGAN AND SOULE—(B) CARBOXYLIC ACIDS AND PHENOL ETHERS—NITROGENOUS BODIES—SULPHUR BODIES—FREE CARBON AND PITCH—SUMMARY—INVESTIGATIONS ON LOW TEMPERATURE TAR OBTAINED ON SEMI-COMMERCIAL SCALE PLANT—MACLAURIN TAR—TAR OBTAINED AT THE FUEL RESEARCH BOARD STATION—SPECIAL PROCESSES FOR THE TREATMENT OF LOW TEMPERATURE TAR—THERMAL DECOMPOSITION OF LOW TEMPERATURE TAR—USES (A) CRUDE OIL, (B) COMPONENTS, (1) TAR ACIDS (2) HYDROCARBONS (3) PITCH (4) BASES.

Low temperature tars differ from one another according to the conditions under which carbonisation is carried out, but, forming as they do, a class distinct in themselves and possessing characteristics common only to tars obtained by the low temperature treatment of coal, it is possible to give a general account of their chemistry and composition. In the subsequent pages, the data given deals almost exclusively with the tar obtained from various bituminous coals, chiefly of the gas and coke-making type, and does not apply to lignites or brown coals.

Low temperature tar will be dealt with under two headings:—

1. *Vacuum Tar*—Obtained by carbonising coal under a greatly reduced pressure and at a temperature usually below 500° C.
2. *Low Temperature Tar Proper*—Obtained by the treatment of coal under normal conditions with regard to pressure and up to a temperature not exceeding about 650° C.

Vacuum Tar

Investigation of the tar obtained by carbonising coal under greatly reduced pressure has done much to elucidate the nature and mode of formation of low temperature tar proper.

The chief investigations upon this type of tar have been carried out, in this country, by Burgess, Jones and Wheeler; on the Continent, by Pictet and Bouvier, Kaiser and Labouchère; and in America by Porter and Taylor.

Jones and Wheeler (Trans.Chem.Soc. 1914. 105. 141) carrying out preliminary work on vacuum tar, failed to find any benzene hydrocarbons in the tar obtained by carbonising coal *in vacuo* up to 430° C., proving conclusively that the tar was very different from ordinary gas or coke oven tar. These results led to further investigations (J.Trans. Chem.Soc. 1914. 105. 2562; 1915. 107. 1318; 1916. 109. 708; 1917. 36. 3) a summary of their results being given below.

Scottish and Durham bituminous coals of the following composition were employed:—

Proximate Analyses of Dried Coals

	Percentage Volatile Matter.	Percentage Ash.
Scottish Coal	26·36	3·28
Durham ,,	30·81	4·10

Ultimate Analyses (Moisture and Ash-free Basis)

	Percentage Carbon.	Percentage Hydrogen.	Percentage Oxygen.	Percentage Nitrogen.	Percentage Sulphur.
Scottish Coal	86·92	4·98	5·56	1·75	0·79
Durham ,,	86·88	5·41	4·71	1·75	1·25

Carbonisation was carried out under a pressure of 5-40 mm. of mercury and approximately 6·5 per cent. of tar of specific gravity 0·967 to 0·999 at $^{15°}/_{15°}$ C., obtained.

Upon fractionally distilling the tar up to 300° C. under ordinary pressure, about 50 per cent. of its weight of soft pitch (sp. gr. 1·128, $^{15°}/_{15°}$ C.) completely soluble in chloroform and containing no free carbon, was obtained, whilst the oils had the following composition:—

(1) Ethylenic hydrocarbons, unsaturated—40-50 per cent.
(2) Naphthenes and liquid paraffins, the former preponderating—about 40 per cent.

(3) Oxygenated bodies, tar acids, consisting chiefly of cresols and xylenols—12-15 per cent.
(4) Aromatic hydrocarbons, probably homologues of naphthalene—about 7 per cent.
(5) Traces of pyridine bases.
(6) A small quantity of a solid paraffin melting at 52·5-54° C., the composition of which approximated to $C_{27}H_{56}$.

The outstanding feature of the above tar is the absence of benzene and its homologues, the large percentage of ethylenic unsaturated hydrocarbons and naphthenes, and the presence of homologues of naphthalene. For further details of the above work, reference should be made to the original literature.

Jones and Wheeler, extracting coal with pyridine and chloroform, obtained :—

(1) A portion insoluble in pyridine and termed the alpha " cellulosic " constituent.
(2) A portion soluble in pyridine but insoluble in chloroform, termed the beta " cellulosic " constituent; and
(3) A portion soluble in pyridine and chloroform, termed the " resinic " constituent.

The first portion yielded on distillation under a vacuum of 5-40 mm., up to 430° C., chiefly phenolic bodies, from which the authors conclude that it is principally the cellulosic constituents which yield the phenols.

Fraction (2) gave somewhat similar oils, of which 40 per cent. were phenolic and the remainder of a " resinic " nature; whilst fraction (3) yielded paraffins, olefines and naphthenes, but no phenols.

The most exhaustive work upon vacuum tar has been carried out by Pictet and his co-workers, who carbonised 1½ tons of a French coal from the Montrambert bed, Loire, under a pressure of 15-20 mm. of mercury and up to a temperature of 450° C., obtaining 60 kilos of tar, upon which their investigations were carried out. (Comptes.rend. 1913. 157. 1436; 1915. 160. 629; Ber. 1915. 48. 926).

The first distillates were obtained at 100° C., and a yield of about 4 per cent. of tar obtained. The tar was of a clear, light brown colour with a slight green fluorescence and a petroleum-like odour, whilst the water collected contained no ammonia, but was distinctly acid. The tar had a specific gravity which gradually increased until it was greater than unity, and, as shown later by Pictet, Kaiser and Labouchère, contained only traces of oxygenated bodies and about 0·2 per cent. of bases. After freeing the tar from these two classes of compounds, the unsaturated hydrocarbons in the residue were removed by shaking with liquid sulphur dioxide, the saturated hydrocarbons remaining being fractionally distilled at atmospheric pressure. In the fractions thus obtained, Pictet and Bouvier isolated the following hydrocarbons belonging to the naphthene series (C_nH_{2n}):—

		Boiling Point under 730 mm. pressure. °C.
C_9H_{18}	Hexahydromesitylene	135-137
$C_{10}H_{20}$		160-161
$C_{10}H_{20}$		172-174
$C_{11}H_{22}$		189-191
$C_{12}H_{24}$		211-229
$C_{13}H_{26}$		227-229

On continuing the distillation under 15 mm. pressure, a small amount of a solid hydrocarbon $C_{30}H_{60}$, melting at 62-63° C. and possessing a specific gravity of 0.9128 at 25° C., was obtained, whilst among the unsaturated hydrocarbons, two were identified:

C_9H_{14} Dihydrotrimethylbenzene boiling at 163-164° C.
$C_{13}H_{16}$,, ,, 240-250° C.

The authors add that probably dihydrogenated derivatives of meta-xylene, of mesitylene and of pseudocumene were present. No naphthalene or anthracene was present, and the residue from the distillation of the naphthenes to 350° C. consisted of an asphalt-like body.

Pictet points out the close resemblance of his naphthenes, not to Baku petroleum oil, which is known to consist largely of these bodies, but to the fractions obtained from certain North American petroleums, examined by Mabery, (J.Amer.

Chem.Soc. 1897. 19. 470; 1903. 25. 267 and 276; 1911. 33. 264) whilst a hydrocarbon $C_{30}H_{60}$, isolated from Galician petroleum, was found identical with the $C_{30}H_{60}$ (melene) in the vacuum tar.

For purposes of comparison, the following table is given :—

Vacuum Tar

Fraction. °C.	Formula.	Density.	Index of Refraction.
135-137	C_9H_{18}	$0·7590^{20°}$	$1·4212^{20°}$
172-174	$C_{10}H_{20}$	$0·7765^{23°}$	$1·4196^{23°}$
189-191	$C_{11}H_{22}$	$0·7838^{22°}$	$1·4234^{22°}$
211-213	$C_{12}H_{24}$	$0·7862^{21°}$	$1·4293^{21°}$
227-229	$C_{13}H_{26}$	$0·7953^{20°}$	$1·4379^{20°}$

American Petroleum

Fraction. °C.	Formula.	Density.	Index of Refraction.
135	C_9H_{18}	0·7591	...
173-174	$C_{10}H_{20}$	0·7770	1.4149
189-191	$C_{11}H_{22}$	0·7832	1·4231
212-214	$C_{12}H_{24}$	0·7857	1·4289
228-230	$C_{13}H_{26}$	0·7979	1·444

Pictet, in conjunction with Kaiser and Labouchère, (Comptes rend. 1917. 165. 113) examined the hydroxy-compounds present, which amounted to 2 per cent. of the tar. They identified hexahydro-p-cresol $C_7H_{14}O$ (B.P. 170-175° C.) together with the following series of unsaturated phenolic bodies :—

Formula of Compound.	Boiling Point °C.
$C_8H_{10}O$	185-190
$C_9H_{12}O$	198-200
$C_{10}H_{14}O$	213-215
$C_{11}H_{16}O$	226-228

In conclusion, it is interesting to note that by cracking this vacuum tar, Pictet obtained " ordinary coal gas," and a tar containing benzene, toluene, xylene, phenols, naphthalene, anthracene, and pyridine bases—in other words a typical high temperature tar.

From the foregoing account of vacuum tar, it will be clearly seen that not only does it differ entirely from ordinary high temperature tar, but that it differs in some respects from low temperature tar proper, produced by carbonising coal at a temperature of 400-600° C. under normal pressure.

Low Temperature Tar Proper

Just as considerable variation is found in the case of the varieties of tar already mentioned, so all low temperature tars differ somewhat from one another in composition. They possess, however, definite characteristics, and after dealing with this class of tar from a general standpoint, a short description of the tars obtained from certain individual processes is given.

Until recently, investigations into the composition of low temperature tars have been almost negligible, and although a general idea of the components was previously known, it is only within the last half-dozen years or so that this scanty knowledge has been expanded to any degree. Low temperature tar is characterised by its low specific gravity, which rarely exceeds 1·08, its low pitch and free carbon content, and the high yield of oils obtained on distillation. The distillates appear to be unstable, readily darkening in colour at normal temperatures.

The constituents of low temperature tar will be dealt with in the following order:—

(1) Hydrocarbons.
(2) Oxygenated bodies—tar acids.
(3) Bodies containing nitrogen and sulphur.
(4) Pitch and " free " carbon.

Hydrocarbons

One of the first comprehensive investigations upon the products of the low temperature carbonisation of American bituminous coals was carried out by Parr and Olin (" The Coking of Coal at Low Temperatures," Bull. 79, Eng. Expt.Stat., University of Illinois). The tar obtained was black to rich brown in colour, possessing an exceedingly disagreeable odour and having a specific gravity of 1·069.

Upon distilling the dehydrated tar, the following fractions were collected:—

Fraction.	Distillation Temperature.	Percentage of Total Tar distilled.
Light Oil	below 210° C.	17·2
Heavy Oil	210-325° C.	52·7
Pitch	above 325° C.	30·1

The light oil possessed a disagreeable odour, was amber in colour, but readily darkened on standing, even in an atmosphere of carbon dioxide. Tar acids and bases were separated by means of caustic soda and sulphuric acid in the usual way, and the following results obtained:—

Light Oil Fraction (to 210° C.)

Specific Gravity 0·966

	Percentage Yield on Basis of Crude Tar.	Percentage Yield on Basis of Light Oil Fraction.
Light Oil Fraction . . .	17·2	100·0
Phenols (and other acid substances)	5·7	33·0
Amines (and other bases) . .	0·9	5·3
Paraffins	3·12	18·1

The refractionation of the light oil, freed from tar acids and bases, gave results shown in the table below :—

Distribution of Neutral Substances in Light Oil

°C.	Fraction.	Percentage Yield on Basis of Light Oil Fraction.	Percentage Yield on Basis of Crude Tar.
75 - 95	Crude Benzol (90 per cent.)	2·10	0·38
95-125	Crude Toluol . .	7·36	1·33
125-170	Crude Solvent Naphtha .	26·30	4·77
170-200	Crude Heavy Naphtha .	14·73	2·67
200-210	Crude Heavy Naphtha .	7·30	1·32

With regard to the above table, Parr and Olin state "Fraction No. 1, besides some benzene, contains also pentanes and hexanes of the paraffin series, ranging in boiling point from 31° C. to 64° C. No. 2 includes some of the heptanes boiling in the nineties. No. 3, according to tables compiled from data obtained by distilling known mixtures, consists of benzene and toluene, the latter preponderating; while fraction No. 4 includes the xylenes boiling from 138° C. to 143° C. with perhaps some mesitylene (B.P. 164° C.) Likewise the part reported as phenols contains besides, one or all of the three cresols, although the close range of boiling point (190°, 201°, and 202°) made a quantitative fractionation of the crude extract impracticable."

The heavy oil (210-325° C.) was a thick, viscous, brown coloured liquid which deposited a non-crystalline sediment on standing; naphthalene and anthracene were absent, whilst the tar acids present contained a large proportion of cresols. The distillation tests are given in the following tables:—

Composition of Heavy Oil

Specific Gravity 1·032

Fraction.	Percentage on Basis of Crude Tar.	Percentage on Basis of Heavy Oil Fraction.
Heavy Oil Fraction	52·7	100·0
Tar Acids	22·2	42·13
Paraffins	6·2	32·66

Distribution of Neutral Substances in Heavy Oil

Fraction.	Percentage on Basis of Crude Tar.	Percentage on Basis of Heavy Oil Fraction.
210-250° C.	2·87	10·3
250-270° C.	13·55	48·5
270°-Pitch	11·53	41·2

The residual pitch from the distillation of the original crude tar was hard, rather brittle, and broke with a bright fracture.

Pitch Fraction (above 325° C.)

Percentage Pitch on basis of Crude Tar	30·1 per cent.
Melting Point	110° C.
Specific Gravity	1·27
Free Carbon	12 per cent.

S. R. Church gives the following analysis of low temperature tar obtained from Vermilion County (Illinois) coal:—

Percentage Water	21·7

Tests on Dry Tar

Specific Gravity at 15·5° C.	1·072
Free Carbon per cent.	1·3
Light Oil to 210° C. per cent. by volume	15·2
Heavy Oil (to Pitch) per cent. by volume	40·2

Light Oil

Tar Acids per cent.	30·0
Sulphonation Residue per cent.	15·0

Heavy Oil

Standard Retort Distillation.	Percentage.
Total per cent. to 170° C.	0·5
200	2·0
210	6·6
235	33·6
270	61·0
315	65·8
355	94·9
Tar acids in total distillate	50·0
Sulphonation residues on fractions	4·5

Pitch

Melting point	76° C.
Free Carbon per cent.	9·0

E. B. Fulks gives the following analysis of a similar tar. The tar was a thick, brown liquid, having a very disagreeable odour:—

Specific Gravity at 38° C.	1·041
Water	trace
Tar acids by volume	27·0 per cent.

Fraction. °C.	
210	10·6 per cent. liquid
235	8·9 ,, ,, ,,
270	12·5 ,, ,, ,,
315	13·1 ,, ,, ,,
355	14·1 ,, ,, ,,
Residue (hard, black, brittle, bright fracture)	40·4 ,, ,, ,,

Paraffin Oil °C.	Fractions.	Percentage of Fraction.	Percentage of Straight Oil.
210	9·7	25·0	2·4
235	9·0	10·0	0·9
270	12·3	10·0	1·2
315	13·7	10·0	1·4
355	15·0	15·0	2·3
	59·8		8·2

Total percentage of paraffins in fractions below 355° C.	13·7
Total percentage of paraffins in fractions below 355° C., based on whole tar	8·2

The general properties of the above tars as well as their composition are very similar to other low temperature tars, with, however, one exception, namely, the presence of benzene and its homologues in the tar. This may be due to the shape of the retort, the temperature to which the vapours evolved were heated, and to the coal employed; the actual temperature of distillation was 400° C.-500° C., i.e., true low temperature carbonisation. In this connection the work of Whitaker and Crowell (J.Ind.Eng.Chem. 1917. 9. 261-269) upon a Pennsylvanian bituminous gas coal is of interest.

As a result of their investigations, they concluded that xylene and toluene begin to form at 400° C., benzene at 500° C., whilst at certain temperatures, maximum yields of these three homologues are obtained, namely:—

Benzene at	800° C.
Toluene at	700° C.
Xylene at	600° C.

Consequently true low temperature tar will contain only small amounts of these substances, whilst as the temperature rises, the quantity of benzene and its homologues in the tar will increase.

Jones and Wheeler (Trans.Chem.Soc. 1910. 97. 1917; 1911. 99. 649) have shown that the evolution of paraffins ceases almost entirely above 700° C., whilst at temperatures below 450° C., ethane, propane, butane, and probably higher members of the paraffin series form a large proportion of the gases evolved, and consequently low temperature tar contains a considerable proportion of paraffin hydrocarbons.

The most comprehensive work on the composition of low temperature tars has been performed by Fischer and Gluud and their co-workers in Germany, and a short abstract of their work will further indicate the nature of this class of tars.

In order to obtain all the light hydrocarbons formed during carbonisation of the coal, the gases evolved were either compressed and thus liquefied, or compressed into paraffin oil, which was then steam distilled to remove the light fractions. The mixture of hydrocarbons thus obtained from the gas and tar was then fractionated, distillation commencing at 20° C., the heavier fractions being distilled either in vacuo or by means of steam.

The results of investigations upon the light hydrocarbons are given in the following tables (Ber. 1919. 52. 1053-1068).

Gas Coal (Lohberg Mine)

150 Kg. coal gave 1850 gms. of light hydrocarbons = 1·23 per cent. yield.

Fraction °C.	Percentage.	Density.
20°-60°	11	$D_8 = 0·6583$
60°-100°	15	$D_{20} = 0·7200$
100°-125°	16	$D_{20} = 0·7684$
125°-190°	40	$D_{20} = 0·8048$
over 190°	10	—
Loss	8	—

Bituminous Coal (Floz Albert, Osterfeld Mine)

150 Kg. coal gave 1000 gms. of light hydrocarbons = ·666 per cent. yield.

Fraction °C.	Percentage,	Density.
20°-60°	8	$D_8 = 0·6651$
60°-100°	13·5	$D_{20} = 0·7180$
100°-125°	20·0	$D_{20} = 0·7873$
125°-190°	45·0	$D_{20} = 0·8214$
over 190°	6·5	—
Loss	7·0	—

Bituminous Coal (Preussiche Clus. Mine, Minden)

150 Kg. coal gave 1520 gms. of light hydrocarbons = 1·0 per cent. yield.

Fraction °C.	Percentage.	Density.
20°-60°	20	$D_8 = 0·6477$
60°-100°	30	$D_{20} = 0·7253$
100°-125°	10	$D_{20} = 0·7711$
125°-190°	33	—
over 190°	5	—
Loss	2	—

As a result of analysis of the different fractions and their chemical behaviour and physical properties, the authors arrived at the following conclusions concerning their composition:

Fraction 20°-60° C. contained saturated paraffin hydrocarbons, probably pentane (C_5H_{12}) and hexane (C_6H_{14}). It is interesting to note that Jones and Wheeler (*vide supra*) detected these hydrocarbons in vacuum tar. Unsaturated hydrocarbons were also present.

Fraction 60°-100° C. This consisted of a mixture of paraffin hydrocarbons, naphthenes, and a small quantity of products of a low hydrogen content. Analysis showed that only a trace of nitrogen and sulphur compounds were present, whilst benzene was absent (compare Parr and Olin, *vide supra*) except as a trace only in the Minden coal.

Fractions 100°-125° C. and 125°-190° C. appeared to consist of a mixture of paraffins, naphthenes, and complex aromatic hydrocarbons.

The fraction boiling between 150° C. and 300° C. from the gas coal (Lohberg), after purifying by means of caustic soda and sulphuric acid, was distilled and a solar oil (150°-220° C.) obtained, whilst the higher fractions yielded motor oil, polishing oil, and gas oils. (Gluud, Ges. Abhandlungen zur Kenntnis der Kohle 1918. 3. 46.) The true composition of the hydrocarbons occurring in these higher fractions is not definitely known, and it seems probable that paraffins, olefines, diolefines, naphthenes, and aromatic hydrocarbons may be present. Fischer and Gluud (*loc. cit.*) isolated from the fraction 200°-320° C. about 10 per cent. of liquid paraffins ranging from $C_{10}H_{22}$ to $C_{19}H_{40}$. These were pále raspberry coloured liquids, possessing a blue fluorescence, whilst each fraction showed slight optical activity. In this connection, it might be mentioned that the joint fractions from vacuum tar were optically inactive; but the benzol extraction of the coal yielded an optically active body (Pictet, Ann. de Chimie 1918. 9. 10. 249-330).

Distillation of the fractions above 300° C. was carried out either under reduced pressure or with super-heated steam, and very thick, viscous oils or solid paraffins obtained. These oils were of the nature of lubricating greases and possessed a viscosity, at 20° C., of 6°-20° Engler, at 50° C., 2°-30° Engler, and a flash point of 120°-200° C. As the temperature increased they became more viscous until the distillates were finally resinous in nature and of a reddish colour.

In the viscous oils and in the red coloured resinous distillate, solid paraffins were present. Gluud (Ges. Abhandlungen zur Kenntnis der Kohle 1917. 2. 301) isolated from these fractions solid paraffin hydrocarbons ranging from $C_{21}H_{50}$ to $C_{29}H_{60}$, hexacosane ($C_{26}H_{54}$) and heptacosane ($C_{27}H_{56}$) preponderating. The amount of these solid paraffins amounted to 0·4 per cent. of the tar obtained from the bituminous coals, and ·1-1½ per cent. of the tar obtained from the gas coal, whilst the melting point ranged from 57° C. to 61° C. These high boiling fractions were decomposed if distilled under ordinary atmospheric pressure. On no occasion was any naphthalene or anthracene isolated from these low temperature tars, and according to Jones (J.Soc.Chem.Ind. 1917. 36. 3) napthalene is only produced by cracking at a temperature of 750° C.

As a result of an investigation carried out upon tar obtained by the Carbocoal process, Morgan and Soule (Chem. Met.Eng. 1922. 26. 923 and 977) have confirmed the work of previous investigators upon the composition of low .temperature tars.

Upon distilling the mixture of crude hydrocarbons (after the removal of tar acids and bases) the first fractions obtained were pale yellow and the higher fractions amber coloured. All the fractions darkened rapidly on standing, finally becoming black in colour. Separation into paraffins, naphthenes and saturated hydrocarbons showed the amount of paraffins present to be much lower than that recorded by other investigators, but with this exception, their results are in close agreement with those previously obtained. Briefly their work may be summarised as follows:—

(1) The hydrocarbons, calculated on the basis of percentage by weight of the tar, consisted of 1·6 per cent. paraffins, 2·8 per cent. naphthenes, and 13·4 per cent. unsaturated hydrocarbons.

(2) Aromatic hydrocarbons, such as benzene, toluene, naphthalene and anthracene were absent.

(3) The unsaturated hydrocarbons were similar in composition to those isolated from vacuum tar by Pictet (*vide supra*).

The absence of naphthalene, but the presence of its derivatives, especially α- and β-methylnaphthalene in low temperature tars has also been confirmed by Fischer and his co-workers (Brennstoff. Chem. 1922. 3. 57) who suggest that the formation of naphthalene in high temperature carbonisation results from the thermal dealkylation or reduction of homologues of naphthalene or naphthol.

Oxygenated Bodies—Tar Acids

These bodies are separated from the tar fractions by agitating the latter with caustic soda solution in which the tar acids dissolve yielding "phenolates." Upon acidifying this solution with as weak an acid as carbon dioxide, the phenols are liberated in the form of dark, brownish red coloured oils containing a quantity of water. The amount of total phenols obtained is much greater in low than in high temperature tars. Although phenol itself is only present in small quantity in the former class, the total amount of tar acids may be as much as 50 per cent. of the tar. Speaking generally, the tar acid content ranges from 25 per cent. to 40 per cent. Further, it would appear that the higher the tar yield, the higher is the percentage of phenols in the tar, whilst Lewes (The Carbonisation of Coal, p. 142) states: " . . . I have noticed that with low temperature carbonisation a coal rich in oxygen invariably gives a tar rich in phenol and cresol, and in a series of low temperature distillations of various coals, made by Bornstein, he found that with high oxygen he obtained large proportions of oxygenated compounds like phenol and cresol, but at the same time the paraffins were low."

Upon fractionating the crude dry phenols at atmospheric pressure, distillates are obtained between 180° C. and 300° C. At this latter temperature, vigorous decomposition begins to take place and the distillation must be continued *in vacuo*. The distillates obtained are yellowish coloured oils which rapidly darken in colour on exposure to the atmosphere, whilst a quantity of pitch remains as a residue.

Owing to the close proximity in boiling point of many of the phenols and to the fact that chemically they behave very similarly to one another, it is extremely difficult to effect the isolation of the different phenols, especially in quantitative yields.

Jones and Wheeler (Trans.Chem.Soc. 1914. 105. 140) concluded that the phenols isolated from "vacuum" tar consisted chiefly of cresols and xylenols, whilst Pictet found none of the lower phenols present in vacuum tar. Upon standing for five years, the tar apparently altered in composition and Pictet isolated from it ordinary phenol, the three cresols and 1.2.4. xylenol, Fischer and his co-workers (Ges. Abhandlungen zur Kenntnis der Kohle 1918. 3. 89: Brennstoff Chem. 1920. 1. 31 and 47) have shown that the quantity of tar acids in low temperature tars may amount to 50 per cent. of the tar. Ordinary phenol was either absent or only present in small quantities—0·06 per cent. in one case—whilst the percentages of other tar acids present were as follows:—

	Percentage.	Range of Distillation.
Cresols	1-2	196°-201° C.
Xylenols	1-2	215°-220° C.
Higher Phenols containing Trimethylphenols	30-32	—
Acid Resins	10	—

The mixture of cresols contained only small quantities of the para-isomer, meta-cresol preponderating in the mixture.

On cracking this tar at 700-750° C., a normal high temperature coal tar containing 1 per cent. of ordinary phenol was obtained.

Another phenol of a different series—catechol $C_6H_4(OH)_2$, a dihydric phenol—was identified in the tar and also in the water separating from it, the quantity isolated amounting to 0·25 per cent. It is noteworthy that this phenol is absent in gas and coke oven tar, though present in the tar obtained from the distillation of brown coal.

The higher boiling fractions, consisting of either highly viscous oils or resinous substances, were composed of complex phenols not yet investigated.

Morgan and Soule (Chem.Met.Eng. 1922. 26. 926) found 14·7 per cent. of tar acids in low temperature tar from the Carbocoal process. Careful distillation of the tar acids yielded the following fractions:—

Fraction.	Temperature °C.	Percentage of Total Phenols.
1	182-189	7·3
2	189-195	6·8
3	195-202	10·8
4	202-207	12·7
5	207-214	8·6
6	214-220	7·9
7	220-227	2·5
8	227-260	18·3
9	260-300	16·5
10	Pitch	8·6
		100·0

The composition of the phenols is given in the following table:—

Component.	Percentage by Weight on Basis of Phenols.	Distillate.	Crude Tar.
Phenol	4·2	1·9	0·6
Cresols	33·4	15·2	4·9
Xylenol Fraction	19·0	8·7	2·8
Higher Homologues	34·8	15·9	5·1
Pitch (and Resins)	8·6	3·9	1·3
	100·0	45·6	14·7

Upon subsequent examination, a large quantity of cresols, in the proportion of 27 per cent. ortho, 19 per cent. meta and 54 per cent. para, was isolated, whilst the higher homologues were found to contain naphthol derivatives, though no α- or β-naphthol was present. It will be observed that the composition of the cresols differs considerably from that found by Fischer, who detected a preponderance of the meta isomer.

Carboxylic Acids and Phenol Ethers

Marcusson and Picard (Zeit.angew.Chem. 1921. 341. 201) have recently recorded the presence of a solid mixture of 13 per cent. phenols and 12 per cent. aromatic carboxylic acids in the low temperature tar obtained from an Upper Silesian coal. This seems to be an abnormal occurrence since no other investigators have discovered even traces of the latter compounds in low temperature tars.

Although both wood tar and peat tar have been found to contain guaiacoal (Aschan, Brennstoff Chem. 1921. 2. 273; E. Bornstein and F. Bernstein, Zeit.angew.Chem. 1914. 271. 71; F. M. Perkin, J.Soc.Chem.Ind. 1914. 33. 395; J.Inst.Pet.Tech. 1914. 1. 76), no trace of either this or any other phenolic ether has been observed in the tar obtained by the low temperature distillation of coal, and it would appear that such bodies are absent from this class of tar.

Nitrogenous Bodies

The proportion of nitrogenous bodies present in low temperature tars is very small, rarely amounting to 1 per cent. of the tar. Jones and Wheeler (Trans.Chem.Soc. 1914. 105. 141) record the presence of traces of pyridine bases in the vacuum tar examined by them, whilst Pictet, Kaiser and Labouchère (Comptes rend. 1917. 165. 113) found 0·2 per cent. of bases in vacuum tar from a French coal. Further investigation showed that primary amines were present, the fraction boiling at 198-203° C. consisting apparently of a mixture of toluidines ($CH_3C_6H_4NH_2$).

Pyridine and other tertiary bases were absent, but a number of saturated secondary bases were isolated and proved to be hydro-derivatives of quinoline and iso-quinoline. The following table shows the boiling points of the higher bases isolated, together with the melting points of their corresponding picrates:—

Formula.	Boiling Point °C.	Melting Point of Picrate °C.
C_7H_9N	198-203	170
C_8H_7N	225	195
C_9H_9N	247-250	184
$C_{10}H_{11}N$	250-260	184
$C_{11}H_{13}N$	260-265	173
$C_{12}H_{15}N$	270-280	166

Parr and Olin (Bull. 79, Eng.Expt.Stat., University of Illinois) report the presence of 0·9 per cent. of "amines" on a basis of the crude tar, in the fraction boiling below 210° C., whilst Gluud (Ges. Abhandlungen zur Kenntnis der Kohle 1918. 3. 227) found 0·46 per cent. of "pyridine bases" in low temperature tar from a gas coal (*vide* p. 174).

Recently, Morgan and Soule (Chem.Met.Eng. 1922. 26. 977) have proved the presence of pyridine in the bases isolated from the low temperature tar produced by the Carbocoal process. The bases consisted of 20 per cent. secondary and 80 per cent. tertiary bases, whilst primary bases were entirely absent. The authors point out that the bases present in the tar are totally different in composition from those present in high temperature tar and suggest that there exist in the higher fractions methylated and ethylated derivatives of hydroquinoline and hydropyridine. The total quantity of bases present amounted to 0·624 per cent. by weight of crude dry tar.

Sulphur Bodies

No thorough examination has been made of the sulphur compounds present in low temperature tars. Sulphuretted hydrogen has been found in samples of this class of tar examined by the authors, and Morgan and Soule (*loc. cit.*) found 0·08-0·1 per cent. present in the first two fractions distilled from a low temperature tar.

They failed to detect carbon bisulphide in the low temperature tar which they examined, whilst the presence of thiophene was uncertain; these compounds are normal constituents of high temperature tars.

It would appear that the organic sulphur compounds present in low temperature tars are, like the nitrogenous compounds, considerably different in composition from those occurring in high temperature tars.

Free Carbon and Pitch

The so-called "free carbon" occurring in tars has been shown to contain elements other than carbon. The amount present varies considerably in the different classes of tars, being greatest in horizontal retort gas tar and present in smallest amounts in vertical retort tar, low temperature tar, and vacuum tar. The "free carbon" is produced by the decomposition of tar vapour on the hot wall of the retort and by the carrying-over of partially distilled carbonaceous material. The quantity of free carbon in a coal tar may amount to as much as 30 per cent. or more, but in low temperature tars it usually lies below 3 per cent. Donath and Asriel (Chem.Zentr. 1903. 1. 1099) give the following composition for free carbon:—

	Percentage Composition.
Carbon	89·2
Hydrogen	2·3
Oxygen	7·13
Nitrogen	0·7
Ash	0·67
	100·00

The value of the pitch is very greatly diminished if it contains a large quantity of free carbon.

The pitch obtained by direct distillation of low temperature tar is much less in quantity than that produced from high temperature tar, rarely exceeding 35 per cent. of the tar distilled, and may be as low as 20 per cent. If distillation is discontinued at 300° C., the pitch is somewhat soft and contains solid paraffins, whilst the product remaining from distillation to 330° C. or thereabouts is much harder, brittle, dark and black, and of a shiny appearance. Decomposition occurs if distillation is carried beyond this point.

Summary of the Composition of Low Temperature Tar

Briefly the composition of low temperature tar may be broadly stated in the following manner:—

Hydrocarbons—about 50 per cent. to 80 per cent., consisting of:

(*a*) Paraffins from the lowest members of the series to members of the series solid at normal temperatures.
(*b*) Naphthenes or hydro-aromatic hydrocarbons, occurring in the fractions above 60° C. and constituting a large proportion of the distillate below 190° C.
(*c*) Unsaturated hydrocarbons—olefinic and cyclic.

Benzene, toluene and their homologues are either absent or only present in small quantities, whilst naphthalene and anthracene are entirely absent.

Oxygenated Bodies—about 20 per cent. to 50 per cent.

These are the tar acids or phenols. Ordinary phenol (carbolic acid C_6H_5OH) is only present in small quantities, the cresols and xylenols each constituting about 1 per cent. to 2 per cent. or more of the tar, whilst higher phenols, of which some are either viscous oils or resinous solids, make up the remainder of the tar acids. Phenols other than those belonging to the monohydroxy series may be present, e.g., catechol.

Nitrogenous Bodies

The substances present containing nitrogen are of two classes: (*a*) basic, (*b*) non-basic. Pyridine is present, but the other bases differ considerably from those occurring in high temperature tar. The total amount present is usually below 1 per cent.

Sulphur Bodies

Sulphur compounds are present in the tar, but no thorough investigation of their composition appears to have been made.

Free Carbon and Pitch

The free carbon is usually below 3 per cent., whilst the pitch obtained by distillation of the tar varies between 20 and 35 per cent. of the total tar.

Investigations on Low Temperature Tar Obtained on Semi-commercial Scale Plant

In the majority of processes, the main object has been the preparation of a satisfactory low temperature coke, and attention has been paid to mechanical detail of plant rather than to the economic utilisation of the tar produced.

The Freeman retort in particular appears to have been designed with due regard to the nature of the tar, special means being taken to obtain oils at the temperature at which they are evolved from the coal.

Maclaurin, whilst aiming at the production of a coke suitable for domestic purposes, has carried out a considerable amount of work upon the utilisation of the tars produced by the Maclaurin process, and recently, the Fuel Research Board has issued details of an examination of low temperature tar produced on the Experimental Plant at East Greenwich. Investigations upon the low temperature tar obtained from the primary retort of the Carbocoal process have already been cited.

Tar Obtained by the Maclaurin Process*

Working with a Cadder coking coal, Maclaurin obtained a dark coloured tar with a setting point of 20° C. and a specific gravity of 1·048. The tar retained water tenaciously, and was of the consistency of butter, in this respect resembling a Mond producer tar. On distillation the following results were obtained :—

Tars from Coking Coal

	Distilled from a Copper Retort.		Distilled from an Iron Retort.
	Percentage.	Specific Gravity.	Percentage.
Oil to 170° C.	3	0·965	6·05
170-230° C.	12	0·968	13·06
Above 230° C.	16	0·992	46·64
Residue	69	1·108	34·25

* Maclaurin (J.Soc.Chem.Ind. 1917. 36. 620)

When a distillation temperature of about 200° C. was reached, it was found that considerable decomposition of the tar resulted, and since "a knowledge of the nature and use of the distillates" was lacking, resolution of the tar into utilisable products by means other than distillation was attempted.

On agitation with paraffin oil, the crude tar separated into three portions, the top layer being a semi-liquid oil, the middle one, water, and the bottom layer a black resinous body. On the addition of weak acid to the top layer, a similar separation was obtained, the bottom layer being a red body of a resinous nature. Washing of the top oil so obtained with a solution of caustic soda and with water gave an oil suitable for lubrication. It is stated that oils prepared in this manner showed no tendency to gum, possessed a low viscosity and compared favourably with pure sperm oil under friction tests, and with a Scotch mineral oil, of specific gravity 0·890, for friction and durability.

The separated resins gave satisfactory yellow, brown and black varnish stains on thinning with turpentine, methylated spirits and benzol respectively. Distillation tests were carried out on the resin in a copper still, with the following results:—

	Percentage.	Specific Gravity.
Water	5·9	—
Oil up to 170° C.	3·35	0·907
170-200° C.	1·55	0·962
200-215° C.	4·65	0·974
215-240° C.	5·80	0·980
240-270° C.	6·00	0·982
270-300° C.	8·30	0·986
300-325° C.	3·60	0·991
325-350° C.	0·20	—
350-370° C.	0·50	—
	39·85	
Pitch	60·15	Sp. Gr. 1·14. Very hard and brittle.
	100·00	

"All the products were quite fluid, but dark in colour, and had an odour like that of solvent naphtha." Decomposition of the resins occurred about 355° C., and distillation as a means of working up was negatived, unless carried out under reduced pressure or by steam. Substances possessing tinctorial properties were obtained by treatment of the tar fractions separated as above.

Tar Obtained at the Fuel Research Station Experimental Retorts

Working with a variety of coals, from 12·9 to 18·4 gallons of crude tar were obtained per ton of dry coal, the tar being fluid at 60° F. and possessing a specific gravity of about 1·05. On cooling, the tar became thicker, at $-5°$ C. being viscous. and solid at $-10°$ C. The tar was distilled, and the separate fractions obtained washed with caustic soda solution (20° Tw.), and concentrated sulphuric acid, the tar acids being separated and purified by distillation. The washed oils were redistilled. The crude tar was found to contain a large proportion of emulsified oil and liquor, and separation of the liquor was obtained by passing the tar through a filter press to remove finely divided suspended matter, and allowing to settle for 48 hours, when the liquor in the tar was reduced to below 3 per cent. On further settling, the liquor was reduced to below 1 per cent. The crude tar had a calorific value of from 16,000 to 16,500 B.Th.U's. per lb. It was found, however, that the flash point of the crude tar was atmospheric, and that by a reduction in the quantity of light spirit, the tar became too viscous at 0° C. to satisfy the requirements of the Admiralty Specification. Furthermore, the crude tar was only miscible in all proportions with a Trinidad oil on the application of considerable heat, shale and American oil not being miscible in any proportions. Burmah, Texas, and American oil only formed stable mixtures with less than 25 per cent. of the crude tar, and Persian with 10 per cent. and under.

By scrubbing the gas with a gas-oil distilling above 210° C., a yield of refined spirit of 1·40 gallons per ton of dry coal was obtained, refining being carried out by washing with concentrated sulphuric acid and caustic soda solution (20° Tw.) and redistilling to 170° C.

Extracts of Results obtained at the Fuel Research Station, East Greenwich, on Experimental Low Temperature Carbonisation Plant.

From Report of The Fuel Research Board for the years 1920, 1921, Second Section: Low Temperature Carbonisation.

Analyses of Tars from Tests in Horizontal Retorts.

Coal.	Dalton Main.				Mitchell Main.		Ellistown Main.	
	1.		2.					
Temperature	550° C.		600° C.		600° C.		600° C.	
Tar:—								
Liquor per cent. (as collected)	20·3		7·0		7·2		7·4	
Tar (dry):—								
Specific Gravity at 15° C.	1·020		1·033		1·036		1·063	
Cal. value B.Th.U's. per lb.	16,650		16,840		16,590		16,020	
Sulphur per cent.	0·45		0·75		0·43		0·96	
Distillation—	% by wt.	Sp. Gr. at 15° C.	% by wt.	Sp. Gr. at 15° C.	% by wt.	Sp. G . at 15° C.	% by wt.	Sp. Gr. at 15° C.
To 170° C.	16·6	0·854	9·1	0·842	10·6	0·840	7·6	0·851
170°-230° C.	13·7	0·975	19·4	0·969	16·1	0·958	18·1	0·980
230°-270° C.	14·1	0·995	12·8	0·998	13·9	0·990	13·8	1·004
270°-310° C.	...	...	11·8	1·027	12·3	1·021	18·1	1·036
270°-350° C.	20·6	1·003	...	...	...	...	...	...
Pitch	30·1	...	46·6	1·197	45·1	...	41·6	...
Loss	5·0	...	0·3	...	2·0	...	0·8	...

Purification of Fractions from Distillation of Low Temperature Tars.

Coal.		Loss on Extraction as Percentages by Volume of Original Fractions.			
		Fraction 1. to 170° C.	Fraction 2. 170-230° C.	Fraction 3. 230-270° C.	Fraction 4. 270-310° C.
Dalton Main 2	Caustic soda	4·0	43·0	40·5	26·0
	Sulphuric acid	7·0	3·0	5·5	6·0
	Washed oil remaining	89·0	54·0	54·0	68·0
	Washed and refined oil	83·0	54·0	51·5	66·1
Mitchell Main	Caustic soda	2·5	43·5	39·0	26·5
	Sulphuric acid	11·5	2·6	5·5	5·5
	Washed oil remaining	86·0	53·9	55·5	68·0
	Washed and refined oil	76·5	51·4	52·2	61·4
Ellistown Main	Caustic soda	7·3	52·0	50·1	36·0
	Sulphuric acid	9·7	4·0	5·4	6·0
	Washed oil remaining	83·0	44·0	44·5	58·0
	Washed and refined oil	70·8	38·7	40·3	51·4

Washed and refined Oils from Tar, calculated to gallons per ton of dry Coal

Coal Carbonised.	Dalton Main 2.	Mitchell Main.	Ellistown Main.
Original yield of tar	14·00	16·25	12·87
Fraction 0-170° *C.*			
Original fraction	1·56	2·13	1·22
Washed spirit	1·39	1·83	1·01
Washed and refined spirit	1·30	1·63	0·86
Fraction 170-230° *C.*			
Original fraction	2·90	2·83	2·53
Washed oil	1·57	1·53	1·11
Washed and refined oil	1·57	1·46	0·98
Fraction 230-270° *C.*			
Original fraction	1·85	2·36	1·88
Washed oil	1·00	1·31	0·84
Washed and refined oil	0·96	1·23	0·76
Fraction 270-310° *C.*			
Original fraction	1,66	2·03	2·39
Washed oil	1·13	1·38	1·39
Washed and refined oil	1·10	1·25	1·23
Total of original fractions	7·97	9·35	8·02
Total washed and refined oils	4·93	5·57	3·83
Total tar acids crude	2·49	2·74	3·20
Total tar acids refined	2·12	2·34	2·58
Pitch. lbs. per ton of dry coal	67·5	75·9	56·9

Specially separated Oils from Dalton Main Tar 2.

	Specific Gravity At 15° C.	Per cent by volume of Tar.	Galls. per Ton of Dry Coal.
Light naphtha to 160° C.	0·829	8·25	1·15
Heavy naphtha, 160-200° C.	0·870	4·59	0·64
Burning oils, 200-270° C.	0·936	11·93	1·67
Gas oil, 270-300° C.	0·979	5·46	0·76
Light lubricating oil, 300-360° C.	1·005	5·10	0·71
Total	—	35·33	4·93

Scrubbing Tests on Low Temperature Coal Gas from Dalton Main Coal 2.

Gas yield :—3,200 c. ft. per ton of dry coal

	Test 1.	Test 2.
Duration of test, hours	8·1	5·0
Gas :		
Total amount scrubbed c. ft.	49·7	60·0
Rate in c. ft. per hour	6·12	12·0
Wash Oil :		
Rate in ccs. per hour	1,394	1,608
Cc. per c. ft. of gas	229	134
Final concentration of spirit, per cent	1·04	1·60
Yield of Spirit :		
Total yield in cc. of crude spirit	118·6	130·8
,, ,, galls. per ton of coal	1.68	1.54
Refined spirit in cc.	102·0	118.0
,, ,, in galls. per ton	1.45	1.39
,, ,, sp. gr. 15° C.	0·731	0·731
Engler distillation of Refined Spirit.		
40° C.	First drop	...
To 60° C.	8·8 per cent.	...
,, 70° C.	23·3 ,,	...
,, 80° C.	42·0 ,,	...
,, 90° C.	56·7 ,,	...
,, 100° C.	68·0 ,,	...
,, 110° C.	77·8 ,,	...
,, 120° C.	85·0 ,,	...
,, 130° C.	91·0 ,,	...
,, 140° C.	94·3 ,,	...
Flask dry at 145° C.	96·0 ,,	...

Special Processes for the Treatment of Low Temperature Tar

Numerous patents have been taken out within recent years for processes designed to obtain marketable products from low temperature tars. Many of these processes deal with the working up of the tar without resorting to distillation, since we have only a partial knowledge of the nature and use of the distillates, and furthermore decomposition of the tar begins at temperatures of about 200° C. They consist essentially of agitation of the crude tar with suitable solvents, whereby a separation of the components of the tar is effected. Such a process has already been described under investigations carried out on the tar produced by the Maclaurin process, and patented by Maclaurin (English Patent 108,339. 1916).

A second method, patented by the same author, (English Patent 108,448. 1916) consists in agitating the tar at 40-50° C. with water containing 3 per cent. by volume of sulphuric acid. On allowing the mixture to settle, three layers are formed, the bottom one consisting of the resinous matter in the tar, the middle one being an acid layer containing the bases, whilst the top layer is composed of hydrocarbon oils.

Maclaurin appears to have been the pioneer in this type of work in England, but in Germany, probably owing to the exigencies of the war with regard to lubricants, motor spirits, oils suitable for Diesel engines, and fuel oil, rapid progress has been made in the manufacture of marketable products from low temperature tars. Fischer and his co-workers figure pre-eminently amongst German investigators.

Many of these processes deal with the preparation of lubricating oils from the tar fractions, e.g., by washing the high boiling fractions with caustic soda or alcohol to remove the tar acids (German Patent 310,653. 11.7.17.). Another method is to heat the tar oils under pressure up to 400° C., or under a reflux condenser, in the presence of suitable catalysts (German Patent 301,775. 19.2.15. and 301,777. 8.4.15.). According to Fischer, Gluud and Breuer (Ges. Abhandlungen zur Kenntnis der Kohle, 1919. 2. 222) it is advisable to remove the phenols before carrying out such a treatment, for although they thicken more rapidly and to a greater extent than the hydrocarbons, there is the possibility that they would continue to thicken when in use, especially if employed as lubricants at somewhat elevated temperatures. The same investigators (*ibid.* 1917. I. 114) also separated the tar into its various constituents by washing with caustic soda to remove phenols, and distilling the residue in superheated steam, dissolving the resulting distillate in acetone. From the acetone solution, the solid paraffins and high boiling oils separated on cooling, whilst the residual acetone solution was fractionated. The following fractions were obtained from the tar:—

	Tar from Bituminous Coal. Percentage Yield.	Tar from Gas Coal. Percentage Yield.	Producer Tar. Percentage Yield.
Viscous Oils (lubricants) .	15·2	10·0	11·3
Paraffin (solid) . . .	0·4	1·0	0·8
Oils (not viscous) . .	33·5	15·0	17·7
Phenols	14·0	50·0	37·8
Resins	4·2	1·0	0·7
Pitch	19·2	6·0	15·0
Loss and Water . . .	13·5	17·0	16·7

A somewhat similar process for preparing lubricating grease from tar or tar oils is described in German Patent 335,189. 22.10.18. The tar is saponified by means of an alkaline lye whereupon a heavy lubricant is obtained. In several patents, hydrogenation under different conditions of temperature, pressure, and nature of the catalyst employed is specified. By such processes it is claimed that the resulting tar oils show a great increase in viscosity over the oils treated.

Space will not allow of a complete description of such processes, but those already cited will serve to show the complexity of the problems associated with the fullest utilisation of low temperature tars.

The Thermal Decomposition of Low Temperature Tar

In view of the utilisation of low temperature tar as a gas-oil or for the manufacture of light spirits suitable for internal combustion engines, the investigation carried out by Jones on the " Thermal Decomposition of Low Temperature Tar " (D. T. Jones, J.Soc.Chem.Ind. 1917. 36. 3.) is of note. The investigation sought primarily to establish the mechanism of the process by which coal tar is formed in the gas retort. The low temperature tar employed had a specific gravity of 0·967 $^{15^\circ}/_{15^\circ}$ C. containing carbon 86·32 per cent., hydrogen 9·53 per cent., and oxygen, nitrogen and sulphur 4·15 per cent. The portion distilling below 300° C. (atmospheric pressure) contained:—

(1) 40-45 per cent. unsaturated hydrocarbons.
(2) Naphthenes.
(3) Approximately 40 per cent. liquid paraffins.
(4) 12-15 per cent. cresols and xylenols.
(5) Homologues of naphthalene.
(6) Traces of pyridine bases and of a solid paraffin, $C_{27}H_{56}$.

The tar was cracked at 650° C. by passing through an electrically heated coke furnace, at the rate of 5 cc.s. per hour. A tar was formed equal to 55 per cent. of the original tar, of a specific gravity 1·043 $^{15}/_{15}$ C. and containing carbon 88·51 per cent., hydrogen 7·18 per cent., oxygen, nitrogen and sulphur 4·31 per cent. Jones compared the two tars, together with the gases evolved at various " cracking " temperatures, and came to the following conclusions:—

(1) Ordinary coal tar is formed from coal at high temperatures, chiefly as the result of the decomposition of a tar previously formed at low temperatures.
(2) The mechanism of this process consists essentially in the decomposition of the naphthenes, paraffins, and unsaturated hydrocarbons, present in the low temperature tar, to form olefines of varying carbon content which condense at higher temperatures to aromatic substances.
(3) The higher (gaseous) olefines are at a maximum at 550° C., practically disappearing at 750° C. At 750° C., naphthalene appears, immediately preceding a rapid increase in the evolution of hydrogen.
(4) Benzene and its homologues are chiefly formed as the

> result of olefinic condensation. To some extent they are secondary products of coal distillation, having been formed by the thermal dehydrogenation of the corresponding naphthenes.

Egloff and Twomey (Chem.Met.Eng. 1916. 15. 245; 1916. 15. 387) have carried out a number of experiments on the cracking of hydrocarbon oils from different sources, such as coal tar and petroleum oils, under varying conditions of pressure, temperature and rate of flow. They have shown that paraffin base oils and naphthene base oils are both suitable for the preparation of benzene, toluene and xylene. The paraffin base oils were cracked at 700° C. under a pressure of 150 lbs. and a maximum total of 12·5 gallons of benzene, toluene and xylene obtained from 100 gallons of oil at a rate of flow of 16 gallons per hour; the maximum quantity of benzene in the recovered oil, viz., 26 per cent., was obtained at a somewhat slower rate of flow; whilst the maximum percentages of toluene (13·8 per cent.) and of xylene (5·9 per cent.) were both produced at the rate previously mentioned. In the case of the naphthene base oils, it would appear that the nature of the starting oil used in the cracking is of paramount importance. The maximum amount of benzene and its homologues obtained are shown in the following table:

Pressure in Atmospheres.	Temperature of Cracking.	Percentage of Aromatic Hydrocarbons obtained				
		Total.	Benzene.	Toluene.	Xylene.	Gasoline.
1	650° C.	14·1	2·6	4·7	6·8	19·3
11	650° C.	18·2	7·2	5·9	5·1	26·2

Since the heavier hydrocarbons in low temperature tar consist mainly of hydrocarbons of the paraffin and naphthene series, the utilisation of these portions of low temperature tar for the production of aromatic bodies of low boiling point, suitable for use in internal combustion engines, appears promising.

Uses for Low Temperature Tar

The claims made by the exponents of the various processes for the low temperature carbonisation of coal, with regard to the utilisation of the tar, must be accepted with considerable reserve. At the same time, it must be realised that low temperature tar and many of the products obtainable from it will not command a special market, but must enter directly into competition with the products obtained from petroleum. Moreover, petroleum products have attained a high standard, and very definite values exist for fuel oil for external and internal combustion, and for various kinds of lubricants. Within limits, this is applicable to the special products obtainable from low temperature tar, as, for example, resins for varnish manufacture and tar acids for the manufacture of disinfectants and for creosoting.

Uses for Crude Tar

(a) As Fuel Oil for External Combustion

The value of low temperature tar as a fuel oil for external combustion has already been established, subject to the investigations with regard to the flash point and viscosity which have been made by the Fuel Research Board. The further utilisation of low temperature tar can be indicated as lying along certain fairly well-defined lines.

(b) As Fuel Oil for Internal Combustion Engines of the Diesel Type.

Constam and Schläpfer have carried out a number of investigations upon the use of different fuels, including tars and tar oils, in Diesel engines (Zeitschrift des Vereines deutscher Ingenieure 1913 Sept. and Oct.). When this research was undertaken, the production of low temperature tar was almost negligible, and the investigations did not include this type of tar. As a result of their work, however, they conclude that tars best suited for use in Diesel engines are those possessing low contents of water, ash, coke, free carbon, and of a fluid nature, and suggest the following specification :—

Ash	trace
Water	below 3 per cent.
Free carbon	„ 3 „
Net calorific value	15,480 B.Th.U.'s per lb.

Low temperature tar could be prepared to meet this specification.

The Anglo-Mexican Petroleum Company (Mex Fuel Oil, p. 144, Philip and Son, London, 1921) having in mind that "while it is true that an engine can be run on almost any heavy oil fuel, the question of the annual repair bill, the time taken for overhaul, and the frequency with which the engine has to be dismantled for cleaning, are important factors, entering largely into the commercial practicability of oil engines," recommend a special Mex Diesel Oil, the specification approximating to the following:—

Specific Gravity at 60° F.	·904
Flash Point closed	over 150° F.
Viscosity R.1 at 40° F.	500 seconds
,, ,, ,, 60° F.	250 ,,
,, ,, ,, 100° F.	85 ,,
Calorific Value	over 19,000 B.Th.U.'s.
Setting point	−35° F.

In the discussion upon a paper by Edgecombe before the Diesel Engine Users' Association (Gas J. 1918. 142. 438), Moore pointed out that the chief factor governing the use of tars and tar oils in Diesel engines was the ignition temperature of the fuel, and whereas petroleum oils possessed an ignition point of below 300° C., tar oils required a temperature approximating to 500° C., necessitating the use of a much greater pressure to ensure ignition, especially when starting the engine up from cold without ignition oil.

Low temperature tar possessing a low viscosity, a low free carbon content, and a high hydrogen content appears applicable for use in engines of the Diesel type. At the same time the high content of oxygenated bodies, with a comparatively low calorific value and an intrinsic value as germicides and disinfectants, makes it advisible to utilise only the hydrocarbon portion of low temperature tar for this purpose. Specifications for fuel oil for use in Diesel engines are given in Appendix I (p. 201).

From a fuel standpoint, Moore places low temperature tars midway between a good grade petroleum crude oil and a heavy gas works tar.

Uses for the Components of Low Temperature Tar

Low temperature tar can be divided broadly into two portions: (1) Tar acids and (2) Hydrocarbons. Separation can be effected either by direct washing of the crude tar with caustic soda solution or by washing the fractions obtained by distillation of the tar. Distillation will give rise to a further product, namely, pitch.

1. USES FOR THE TAR ACIDS

Tar acids are used in large quantities for creosoting timber. According to Coffin (Gas Age Record. 1921. 48. 3. 97), the tar acids obtained from low temperature tar have a greater preserving action for timber than ordinary high temperature tar creosote, despite the fact that no naphthalene is present in such tar. If these tar acids possess the preserving property ascribed to them by Coffin, a large quantity should find application for this purpose. America used 90 to 100 million gallons of creosote oil for the preservation of timber during 1913, of which two-thirds was imported.

One of the chief uses for the low fractions obtained from the crude tar acids is for the production of different grades of disinfectants and insecticides. According to Ditthorn (J.Soc.Chem.Ind. 1920. 39. 799 A.; Centr. Bakt. 1918. 1. 82. 483) m-cresol is a more powerful germicide than the other two isomers—a fact of particular interest since, according to Fischer, the m-cresol isomer preponderates in the crude cresylic acid fraction. Furthermore, the cresols and xylenols, though possessing more marked antiseptic properties than ordinary phenol, are not so poisonous, and consequently are better suited to the purpose.

The nature of prepared disinfectants can be seen from the following short descriptions of a few of the better known ones, but, as a rule, every maker has a formula of his own, each differing slightly from one another.

Liquid Disinfectants.

(1) Creoline.

This is prepared by saponifying resin with caustic soda solution (sp. gr. about 1·332) at 100° C., adding the tar oil previously heated to a temperature of about 70-80° C., mixing the whole well together and filtering.

The product contains 2·5-4·5 per cent. of caustic soda and

65-80 per cent. of coal tar oil. Lunge gives the following as typical analyses of different samples of creoline:

	Caustic Soda Content.			Percentage Coal Tar Oil.	B.P. of Tar Oil. °C.	Percentage Phenols Cresols.	Percentage Rosin.
	Percentage unsaponified.	Percentage saponified.	Total.				
Creoline A .	1·76	0·96	2·72	77	180-270	12	17·5
Creoline B .	2·96	0·32	3·28	66	170-260	16	27·3
Creoline Italian	1·84	0·76	2·60	76	160-270	16	19·0

(2) Lysol.

Lysol is made from tar acids, usually phenol or the cresols, or from tar oils rich in tar acids. The phenols are treated with soya bean, linseed or cocoanut oils and the mixture saponified with caustic soda or potash, a small quantity of alcohol being added to increase the solubility of the disinfectant in water. Reuss gives the following analyses of two brands of lysol :—

	Percentage Composition.	
Pure cresols	49·20	44·58
Impurities in the cresols . .	·76	4·40
Potassium linoleate . . .	19·80	27·83
Glycerine from the soap . .	2·13	3·48
Glycerine added . . .	—	4·12
Water	21·34	9·32
Ash	6·51	7·17

Other disinfectants of a somewhat similar nature to the above are lysocresol, lysoform containing formaldehyde, saprol, etc.

Disinfecting powders are made from phenol or cresols mixed with a certain amount of a suitable filler, such as hydrated lime, calcium sulphite, China clay, magnesium chloride and similar substances.

Bakelites

One of the most interesting outlets for the lower tar acids is in the manufacture of what are known as Bakelites, after the inventor Baekeland. The manufacture of these substances is based upon the fact that phenol or the cresols and other bodies can be condensed with formaldehyde, preferably with the aid of certain condensing agents, to give resinous-like bodies of varying consistency. As early as 1872, Baeyer had obtained condensation products of a resinous nature from phenol and formaldehyde, but it was only in 1907 that Baekeland, by discovering that the presence of a small amount of an alkaline condensing agent greatly assisted in the formation of the resinous product, that the process could be worked on a commercial scale. By varying the method of manufacture, different products can be obtained, some being very hard, fusible substances, soluble in the usual organic solvents, whilst others are hard, infusible and insoluble. The pure bakelite is either a colourless, yellow, or brown, semi-transparent solid, resembling shellac. It is an excellent insulator, both for heat and electricity, having a dielectric strength of 23,000 volts per millimetre thickness. Besides being used in the manufacture of such articles as knife handles, buttons, pencil-cases, etc., it can also be used for impregnating sawdust, cellulose, asbestos powder, and similar materials, which are subsequently made up into such articles as cases, reels for electrical purposes, photographic dishes, etc. A very brilliant varnish can be produced on the surface of wood by impregnating it with bakelite and subsequently heating it under pressure, whilst a bakelite varnish can be made from the soluble variety dissolved in methylated spirits. For further information on this interesting subject, the following articles should be consulted:

J.Ind.Eng.Chem. 1909. 1. 149 and 545; 1913. 5. 506; 1921. 13. 135.
Trans.Amer.Elect.Chem.Soc. 1909. 15. 597.
J.Soc.Chem.Ind. 1913. 32. 559 and 1921. 40. 398A.
Chem.Met.Eng. 1921. 24. 661.
Sitzungsber Preuss.Akad.Wiss. 1918. 1201.
Ges. Abhandlungen der Kenntnis der Kohle 1919. 4. 221.

2. THE HYDROCARBONS OBTAINED FROM LOW TEMPERATURE TAR

The hydrocarbon portion of low temperature tar will, in all probability, eventually yield distillation products similar to those obtained from crude petroleum. Crude petroleum yields:—

(1) Various qualities of spirit, suitable for use in petrol engines and as solvents, etc., and distilling between 60-150° C.

(2) Oils, suitable for illuminating purposes and for engines fitted with vaporisers, and distilling between 150-300° C.

(3) Solar and gas oils, for the production of gas for enriching purposes and as fuel for heavy oil engines.
(4) Still residuum for use in engines of the Diesel type or for the manufacture of lubricants and asphalt or coke.

The yield of products comparable with the above petroleum products will vary according to the type of coal carbonised, and the method of carbonisation.

For the refining of the light oil obtained from low temperature tar and suitable for motor spirit, new methods may be developed beyond those at present in use in the refining of the corresponding petroleum fractions, designed to materially increase the yield. Cracking of certain portions of the tar will probably figure largely in any such methods.

Fischer (Brennstoff Chem. 1921. 2. 327, 347) outlines methods whereby the yield of motor spirit per ton of coal carbonised can be increased. He states that it is possible to obtain 5·25 per cent. by weight of motor spirit from gas coal made up in the following manner:—

Stripped from the gas	0·35	per cent.
Distilled from the tar	1·00	,,
By cracking of the tar	0·80	,,
Crude benzol from the tar acids, by passing through tinned iron tubes filled with turnings of tinned iron and maintained at 700-800° C. in the presence of excess of hydrogen .	2·00	,,
Alcohols obtained from conversion of unsaturated compounds	1·20	,,
	5·35	,,

The oil available as motor spirit may be taken as approximating to three gallons of motor spirit per ton of bituminous coal carbonised.

At the present time, there exists no standard practice for the working up of the hydrocarbons oils from low temperature tar, such as exists for the working up of gas works tar by the tar distiller.

Not only are further investigations required upon the nature of the hydrocarbons present in low temperature tar before such standard practice will be evolved, but also a new aspect of tar distillation will have to be developed, the tar distiller not being willing to modify his plant and practice to the working up of such tar.

A case which has come to the authors' notice, in which samples of low temperature tars were submitted to a tar distiller for a commercial valuation, serves to emphasise the attitude adopted, the distiller classifying the tars as producer tars.

The pitch produced by distillation resembles petroleum asphalt, and should find employment for the construction of road surfaces, etc. Judged on its free carbon content it would find use as a binder for the manufacture of coal briquettes.

The bases obtained from low temperature tar (e.g., pyridine, picolines and lutidines) may find a use as denaturing spirit, and for the manufacture of special solvents.

APPENDIX I

SPECIFICATIONS

British Admiralty Fuel Oil Specification

The oil fuel supplied shall consist of liquid hydrocarbons, and may be either:—

(*a*) Shale oil; or
(*b*) Petroleum, as may be required; or
(*c*) A distillate or a residual product of petroleum; and shall comply with the Admiralty requirements as regards flash point, fluidity at low temperatures, percentage of sulphur, presence of water, acidity, and freedom from impurities.

The flash point shall not be lower than 175° F., close test—Abel or Pensky-Martens. In the case of oils of exceptionally low viscosity, such as distillates from shale, the flash point must not be less than 200° F. The proportion of sulphur contained in the oil shall not exceed 3 per cent. The oil fuel supplied shall be as free as possible from acid, and in any case the quantity of acid must not exceed ·05 per cent. calculated as oleic acid when tested by shaking up the oil with distilled water, and determining by titration with decinormal alkali the amount of acid extracted by the water, methyl orange being used as indicator. The quantity of water delivered with the oil shall not exceed ·5 per cent.

The viscosity of the oil supplied shall not exceed 2,000 seconds for an outflow of 50 cubic centimetres at a temperature of 32° F., as determined by Sir Boverton Redwood's standard viscometer (Admiralty type for testing oil fuel). Pending settlement of this specification, a viscosity of 1,000 seconds was provisionally adopted in 1912. The oil supplied shall be free from earthy, carbonaceous, or fibrous matter or other impurities which are likely to choke the burners. The oil shall, if required by the inspecting officer, be strained by being pumped, on discharge from the tanks or tank steamer, through filters of wire gauze having 16 meshes to the inch.

British Standard Specification for Benzol for Motor Fuel

The complete Standard Specification for Benzol for Motor Fuel is published by The British Engineering Standards Association, Report No. 135, 1921, (Crosby, Lockwood & Son) from which the following details are abstracted by the courtesy of the Association.

Definition

1. The term benzol shall denote a liquid consisting essentially of a mixture of benzene and not more than 30 per cent. by volume of toluene and xylenes.

Description

2. The material shall be a clear water white liquid free from undissolved water and other visible impurities.

Specific Gravity

3. The specific gravity at 15·5° C. (60° F.) shall not be less than 0·870 and not more than 0·885.

Distillation Range

4. When 100 c.c. of the material are distilled in the Standard Distillation Apparatus at a rate of 7 c.c. per minute, there shall distil at 760 mm. pressure: —

Not less than 60 c.c. at or below 90° C. (194° F.).
Not less than 75 c.c. at or below 100° C. (212° F.).
Not less than 90 c.c. at or below 120° C. (248° F.).

The flask shall be dry at a temperature not exceeding 125° C. (257° F.). The temperature recorded by the thermometer shall be corrected for emergent stem and barometric pressure.

Residue

5. The amount of non-volatile residue remaining when 20 c.c. of the material are evaporated, and subsequently heated for two hours on a water bath at 100° C. (212° F.) shall not exceed 0·01 per cent. by weight.

Coloration with Sulphuric Acid

6. The coloration imparted to pure sulphuric acid (90 per cent. H_2SO_4) free from nitric acid, when 90 c.c. of the material are shaken with 10 c.c. of the acid for five minutes at ordinary temperatures shall not be more than a light brown.

Sulphur Content

7. The total sulphur content shall not exceed 4 per cent. by weight.

Freedom from Acid and Alkali
8. The material shall give no reaction for free acid or free alkali.

Freedom from Sulphuretted Hydrogen
9. The material shall give no reaction for sulphuretted hydrogen.

Freezing Point
10. The freezing point shall be not higher than −14° C. (7° F.).

In the complete specification details are given of the methods of carrying out the tests mentioned above.

British Standard Specification for Tar and Pitch for Road Purposes

The complete Standard Specifications for Tar and Pitch for Road Purposes are published by the British Engineering Standards Association, Report No. 26, 1916, (Crosby, Lockwood & Son), from which the following details are abstracted by the courtesy of the Association.

TAR NO. 1. Based upon the Road Board Specification Nos. 4 and 5—suitable for surface tarring of roads.

Source
The tar shall be derived solely from the carbonisation of coal, except that it may contain not more than 10 per cent. by volume of carburetted water gas tar or distillates or pitch therefrom.

Specific Gravity
The specific gravity of the tar at 15° C. shall not be less than 1·16 and not more than 1·22.

Distillation Range
On distillation in a litre fractionation flask without special fractionation column, one-half to two-thirds filled, the tar shall yield:—

Not more than 1 per cent. of distillate below 170° C.
Not more than 26 per cent. and not less than 16 per cent. of distillate between 170°-270° C.
Not more than 10 per cent. and not less than 3 per cent. of distillate between 270°-300° C.
Not more than 34 per cent. and not less than 24 per cent. of total distillate between 170°-300° C.

Naphthalene
The fraction 170-270° C. on standing at 30° C. for half an hour shall deposit no solid matter (naphthalene, etc.).

Phenols
The fraction 170°-270° C. on treatment with caustic soda solution shall not yield more than 3 per cent. by volume of the tar of crude tar acids.

Free Carbon
The tar shall contain not less than 12 per cent. and not more than 24 per cent. by weight of free carbon.

Water and Ammoniacal Liquor
The tar shall not contain more than 1 per cent. by volume of water in excess of 5 grains of ammonia per gallon.

TAR NO. 2. Suitable for making tar macadam and for surface spraying when road crust is very dry.

Source
The tar shall be derived wholly from the carbonisation of coal, except that it may contain not more than 25 per cent. by volume of carburetted water gas tar or distillates or pitch therefrom.

Specific Gravity
The specific gravity of the tar at 15° C. shall not be less than 1·19 or more than 1·24.

Distillation Range
On distillation in a litre fractionation flask without special fractionation column, one-half to two-thirds filled, the tar shall yield:—

Not more than 1 per cent. of distillate below 170° C.
Not more than 18 per cent. and not less than 12 per cent. of distillate between 170°-270° C.
Not more than 10 per cent. and not less than 6 per cent. of distillate between 270°-300° C.
Not more than 26 per cent. and not less than 21 per cent. of total distillate between 170°-300° C.

Naphthalene
The fraction 170°-270° C., on standing at 25° C. for half an hour shall deposit no solid matter, (naphthalene, etc.).

Phenols
The fraction 170°-270° C., on treatment with caustic soda solution, shall not yield more than 2 per cent. by volume of the tar of tar acids.

Free Carbon
The tar shall contain not less than 12 per cent. and not more than 22 per cent. by weight of free carbon.

British Standard Specification for Pitch Suitable for Pitch Grouting (Ref. Road Board General Directions for Pitch Grouting)

PREPARED PITCH FROM TAR DISTILLERS
The pitch shall not yield more than 4 per cent. of distillate below 270° C. and shall not contain less than 16 per cent. and not more than 28 per cent. of free carbon.

COMMERCIAL SOFT PITCH
Source
The pitch shall be wholly derived from tar obtained from the carbonisation of coal, except that it may contain not more than 25 per cent. of pitch obtained from carburetted water gas tar.

Distillation Range
Not more than 1 per cent. of distillate below 270° C.
Not more than 5 per cent. and not less than 2 per cent. of distillate between 270°-315° C.

Free Carbon
The pitch shall contain not more than 31 per cent. and not less than 18 per cent. of free carbon.

The pitch should be of such a consistency as will give a penetration of 70 at 25° C., when tested on a penetrometer with a No. 2 needle weighted to 100 gms. for five seconds. If the pitch is not of a suitable consistency, it may be prepared by the addition of tar oil to commercial soft pitch.

TAR OIL
Source
The tar oil should preferably be a filtered green or anthracene oil, and must be derived wholly from tar produced in the carbonisation of coal, or from such tar containing not more than 25 per cent. of its volume of carburetted water gas tar.

Specific Gravity
The specific gravity of the tar oil at 20° C. shall not be less than 1·065 and not more than 1·085.

Naphthalene and Anthracene
The tar oil on standing at 20° C. for half an hour, shall remain clear and free from solid matter.

Distillation Range
The tar oil shall be commercially free from light oils and water.

On distillation in a litre fractionation flask without special fractionating column, one-half to two-thirds filled, the tar shall yield:—

Not more than 1 per cent. of distillate below 170° C.
Not more than 30 per cent. of distillate below 270° C.
Not less than 95 per cent. of distillate below 300° C.

Specifications of Tar Oil for Use in Diesel Engines

(1) *Rath and Rossenbeck.* (Gluckauf, 13th May, 1911.) For the German Tar Distillers' Federation.

1. The tar oils must not contain more than 0·2 per cent. of solid constituents insoluble in xylol. The incombustible constituents shall not be more than 0·05 per cent.
2. The water content must not exceed 1 per cent.
3. The coke residue shall not exceed 3 per cent.
4. In the distillation test at least 60 per cent. by volume must distil over up to 300° C.
5. The net calorific value shall be not less than 8,800 cals. per kilogram.
6. The flash point must not be under 65° C.
7. The oil must flow freely at 15° C. On cooling the oil to 8° C., and allowing to rest at this temperature for half an hour, no separation shall take place.

(2) *Augsberg-Nurnberg Co.* (Porter. Meeting of the Diesel Engine Users' Association, 24th May, 1917).

1. The tar oil must be a distillate of coal tar.
2. The oil must flow freely at 61° F., and on being cooled down to 46·5° F. and resting in a place undisturbed by vibration, no separation shall take place at this temperature within the space of half an hour.
3. The following constituents shall not be present in greater quantities than the stated percentages:—

Ash	... 0·05 per cent.
Sulphur	... 1·0 ,,

4. Percentage insoluble in xylol 0·2 per cent.

Proportions of water and coke residue not stated.

(3) *Day*. (Meeting of the Diesel Engine Users' Association, January, 1916.)

1. The tar oil must be a product of the distillation of coal tar. No product which has not undergone distillation must be used.
2. The tar must not contain more than 2 per cent. solid constituents insoluble in xylol.
3. The ash content must not be greater than 0·08 per cent.
4. The water content must not be greater than 2·5 per cent.
5. The coking residue must not exceed 3 per cent.
6. The oil must be liquid at 60° F. when maintained at that temperature for half an hour.
7. In case of crystals settling in the transport tank, the buyer to be allowed to drain off the liquid portion and return the solid to the sender.

6 and 7 may be omitted.

(4) *Batho*. (Meeting of the Diesel Engine Users' Association, 23rd February, 1916.)

1. Specific gravity	Between 1·0 and 1·1.
2. Viscosity	Generally 2° Engler (all coal tar oils are very fluid).
3. Flash point	100° F. to 130° F.
4. Colour	Tar oils are as a rule dark to almost black. One drop on white paper should show no black residue as is the case with tar. This black residue means a large percentage of free carbon or other tar ingredients.
5. Lower calorific value	Between 15,800 and 16,500 B.Th.U's. per lb.
6. Ash	Should not exceed 1 per cent. (unburnt residue of tar oil is mostly harmless).
7. Water	Should not exceed 1 per cent.
8. Sulphur	·5 per cent. to 1·0 per cent.
9. Pitch	If the tar oil contains a high percentage of residue which only begins to vaporise at 400° C., then the same results can be expected as with the tar; i.e., one must anticipate a considerable amount of dirt in the engine, and the exhaust valves will require frequent cleaning and grinding in.

APPENDIX II

The Structure of Coke and its Combustibility

The complex nature of the decomposition of coal renders the study of coke formation extremely difficult, and the influence of the structure of carbonised fuels upon their combustibility is difficult to determine owing to the complexity of the phenomena of combustion.

The importance of structure in this connection has only recently been realised, and the researches of Beilby,* Sutcliffe and Evans,† and Greenwood and Cobb‡ mark the commencement of systematic study upon this subject.

Microscopical examination of coke sections prepared after the manner employed by Lomax, whilst showing the open nature of coke do not adequately indicate the nature of the minute cellular structure of the coke, a fact evidenced by an examination of the preparations of Wilhelm Thörner (Stähl und Eisen. 1886. 6. 17.) in which the sections were photographed by transmitted light. On the other hand, microphotographs of "an untouched broken surface" of the coke show clearly this cellular structure. By an examination of such microphotographs, Beilby concludes that "coke structure, however minute, is due to the evolution of gas bubbles from the fused or partially fused coal substance," and places the formation of coke into stages:—(1) Fusion of the coal forming a foam, in which the bubbles of gas formed by the decomposition of the fused mass, are each self contained cells; (2) By the "mutual perforation of these bubble cells at their points of contact, a sponge is produced through which the gases ultimately escape to the outside of the mass"; and (3) "With increased temperatures the formation of a rigid spongy mass, in the walls of which by further decomposition, more minute cells are formed." He further draws a striking contrast between the behaviour of the coal substance and sugar on carbonisation.

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* Sir George Beilby—The Structure of Coke: Its Origin and Development.—J.Soc.Chem.Ind. 1922. 41. 341T.

† E. R. Sutcliffe and Edgar C. Evans—The Influence of Structure on the Combustibility and other Properties of Solid Fuels.—J.Soc.Chem.Ind. 1922. 41. 196T.

‡ H. D. Greenwood and J. W. Cobb—The Structure of Coke.—J.Soc.Chem.Ind. 1922. 41. 181T.

In the case of sugar, evolution of gas and frothing fell off rapidly at 350° C. and practically ceased at 400° C., no change in structure being noted beyond that temperature. Such conclusions directly contradict those of Thörner, who stated that the cell walls of coke consisted of "an extremely close impermeable glassy mass," whereas they possess a minute sponge cell structure and a porosity comparable to and even exceeding that of charcoal. Sutcliffe and Evans, by a preliminary pulverisation of coal to dust of a fineness "comparable with that required for dust firing," followed by briquetting and carbonisation, have prepared an activated carbon which will absorb 10 per cent. of its weight of heavy vapours.

Beilby shows that the carbon forming the cell walls of a coke is a vitreous glass-like material, vitrification becoming more pronounced as the temperature to which the coke is submitted increases, the "vitreous state becoming more and more marked as the state of elemental purity is reached."

In considering the influence of structure upon the combustibility of a fuel Sutcliffe and Evans outline the principal factors as follows:—

(1) *Influence of area of surface*

". . . Combustion can only be maintained if the area of incandescent surface exposed to the air is sufficient to maintain the temperature of a sufficient mass of fuel above the point of ignition. The area of surface of blast furnace coke, for example, is much greater than that of a lump of anthracite, and the combustibility of the coke is, therefore, greater. . . . Charcoal, with its highly developed cell structure, is a fuel possessing a very considerable area of surface per unit of mass, and is characterised by a high degree of porosity.

"Area of surface . . . is closely connected with degree of porosity, and with the character and distribution of the pores."

(2) *Porosity*

". . . Very considerable differences exist between the degrees of combustibility of fuels of equal porosity, and on investigation it will be found that it is a question not so much of the total air space in a fuel as of the number of cells it contains and of the ways in which these cells are interconnected. In this connection it is important to consider the porosity of the cell walls. . . ."

(3) *Character of cell structure* (*a*) *Continuity of cell structure*

"Thörner found that Meiler coke and charcoal, the fuels best suited for use in blast furnaces, contained cells regularly arranged and joined to one another longitudinally, whereas blast furnace coke contained discontinuous groups of cells, the walls of which were of vitreous carbon. Carrick Anderson (J.Soc.Chem.Ind. 1896. 15. 20) and Anderson and Roberts (J.Soc.Chem.Ind. 1899. 18. 1102) were of the opinion that the cells were gas-tight, the walls being vitreous and impermeable. Taking a general view of this work it might be perhaps too much to say that the cell structure of blast-furnace coke is discontinuous; after all, the gases evolved in the later stages of distillation must get away, but there is reason to believe that the cells are connected by passages of small diameter as compared with the diameter of the cells. Further there is every reason to believe that the walls of these cells have been rendered vitreous and gas-tight by carbon deposition."

The cells in charcoal lie longitudinally through the mass, whilst the authors state that the continuity of the cell structure in fuel briquetted prior to carbonisation is more pronounced than in cokes produced at high temperatures.

(*b*) *Effect of size of cells*

The size of the cells has a direct bearing upon the combustibility of the coke. Low temperature coke prepared by the usual methods (as distinct from methods entailing either blending or preliminary pulverisation and briquetting) possess a low apparent specific gravity, i.e., they are very voluminous, and whilst they may contain a large number of large cells per unit mass, contain also only a small number of large cells per unit volume. Combustibility of such coke is high, but at the same time it is fragile and will not withstand excessive handling, and is entirely unsuited for blast furnace purposes. "The most desirable fuel would be a fuel as dense as possible, but containing a large number of cells per unit mass." Dependent upon the degree of grinding prior to briquetting and carbonising, it has been found possible to vary the density and combustibility of the resulting fuel, the more finely divided the coal the more dense and more combustible the resulting product.

Other factors influencing the combustibility of any carbonised fuel are the presence of volatile matter, the formation of a graphitic film at high temperatures, the temperature and pressure at which carbonisation is effected and the nature of the fuel carbonised.

Greenwood and Cobb by an examination of the real and apparent specific gravities and porosities of cokes prepared at various temperatures, divide the formation of high temperature coke from a Nottinghamshire gas coal into three stages:—

(1) Up to 550° C.—A stage in which initial cell formation takes place, the cells having relatively thick walls of soft material of low specific gravity, the mass of coal swelling during this period.

(2) 550-850° C.—The walls of the cells become thinner, but stronger and marked shrinking of the mass takes place with an increase in specific gravity. The porosity of the material reaches a maximum.

(3) 850° C. upwards.—There is no appreciable increase in specific gravity during this stage, but contraction of the mass is the predominant feature, and a coke with relatively thick walls and small pores is obtained.

At no stage does the specific gravity of the material approximate to that of graphite (2·3).

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MICROPHOTOGRAPHS OF COKE STRUCTURE.

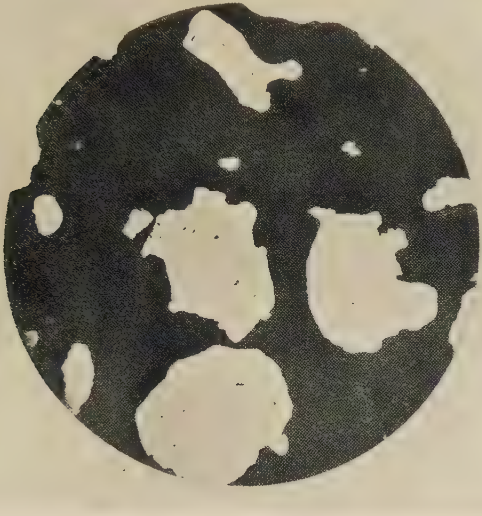

Fig. 26.

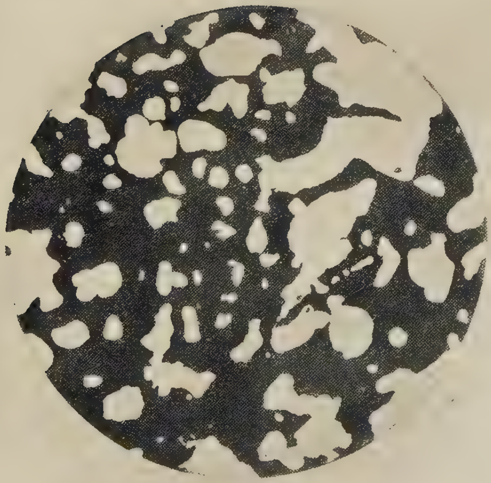

Fig. 27.

Fig. 26. Gas Retort Coke. × 50.—Dr. Thörner, "Stahl und Eisen," 1886.

Fig. 27. Metallurgical Coke. × 50.—Dr. Thörner, "Stahl und Eisen," 1886.

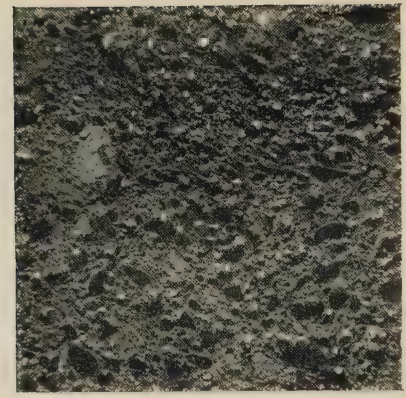
FIG. 28.

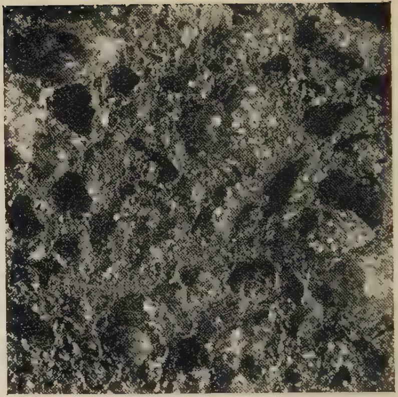
FIG. 31.

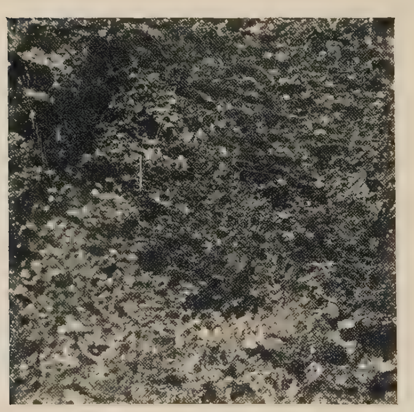
FIG. 29.

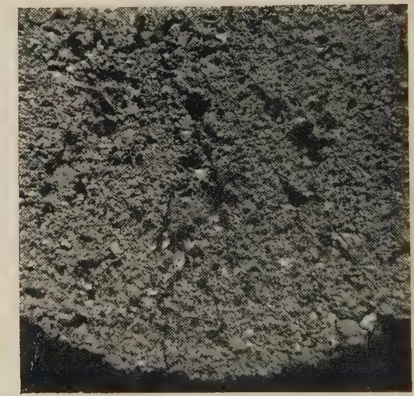
FIG. 32.

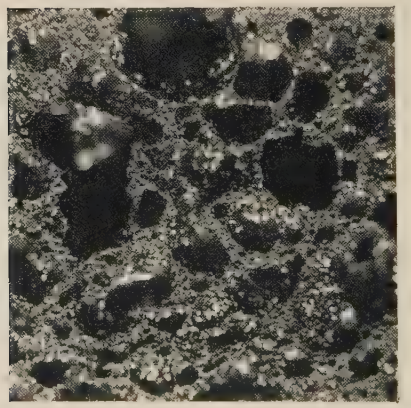
FIG. 30.

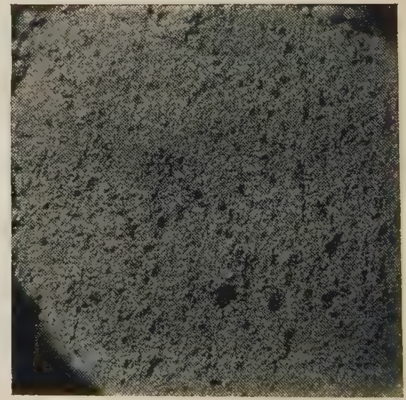
FIG. 33.

FIG. 28. Gas Coke from Durham Coal carbonised in Horizontal Retorts. × 5–10. FIG. 29. Blast Furnace Coke from Recovery Ovens (Compare Figs. 26 and 27). × 5–10. FIG. 30. Coke from fairly fusible Coal (Mitchell Main Coal—Froths on Carbonisation) (Compare Fig. 40 C). × 5–10. FIG. 31. Coke from Arley Coal carbonised in Vertical Retorts (Compare Enlargement, Fig. 34). × 5–10. FIG. 32. Cross Section—Coke from Dalton Main (Compare Figs. 40 A, 40 B). × 5–10. FIG. 33. Coke from Carbonisation of Briquette made from Pulverised Coal (Compare Fig. 35). × 5–10.

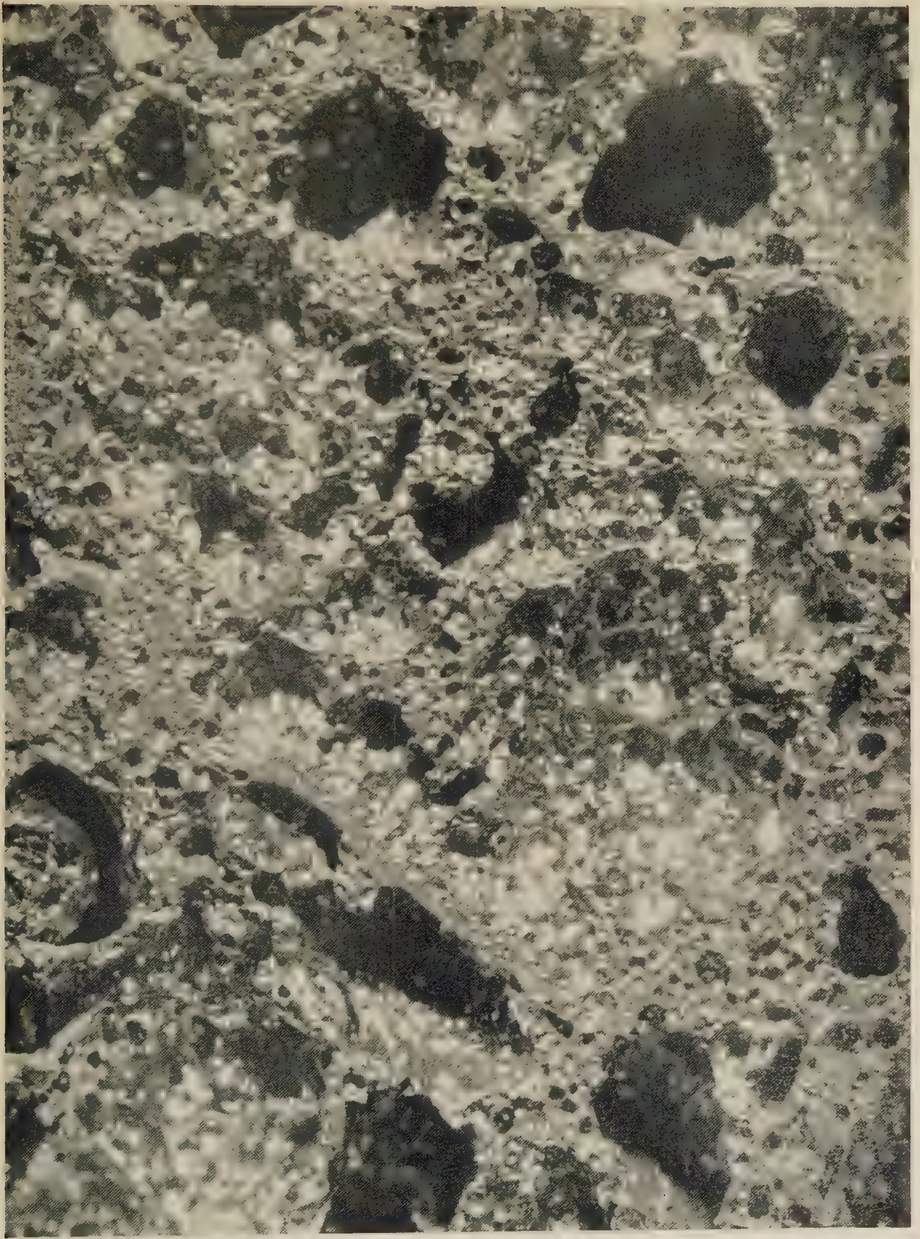

Fig. 34.

Enlargement of Fig. 31—Coke from Arley Coal carbonised in Vertical Retorts with Steaming. Note Continuity of Bubble Sponge Structure.

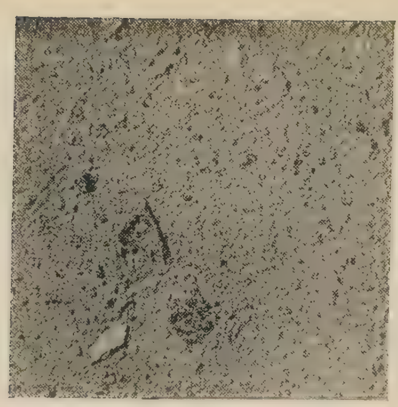

FIG. 35.

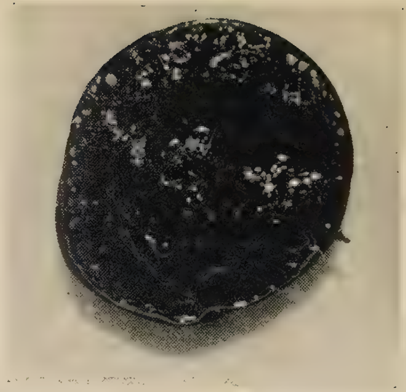

FIG. 36.

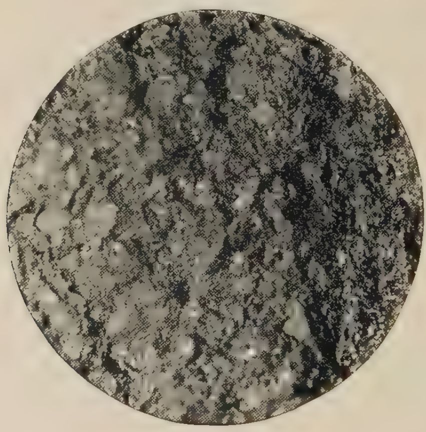

FIG. 37.

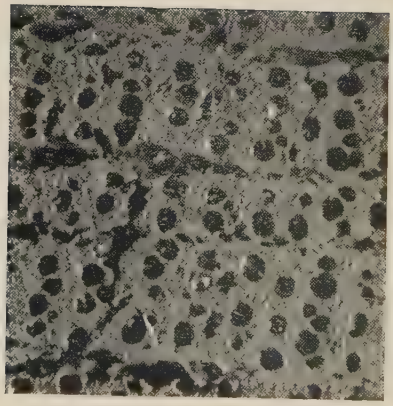

FIG. 38.

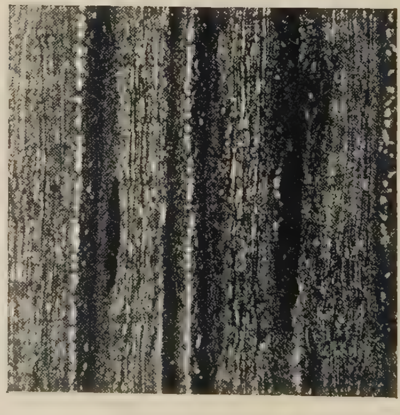

FIG. 39.

FIG. 35. Coke from Mitchell Main and Ellistown Main Coals, blended and briquetted. (Temperature of carbonisation higher than that employed in Fig. 33). × 5–10. FIG. 36. Vitreous Carbon from Sugar. (Note absence of Minute Coke Structure.) FIG. 37. Broken Surface of Briquette made from Pulverised Coal. Heated to 380° C. Compression 2 tons per sq. in. × 5-10. FIG. 38. Oak Charcoal—Section across grain of Wood. × 5-10. FIG. 39. Oak Charcoal—Section along grain of Wood. × 5–10. (Note Figs. 38 and 39—No evidence of fusion and bubbling. Structures show reproduction of Natural Cell-structure of Wood.) × 5–10.

COKE PRODUCED IN LABORATORY ASSAY APPARATUS: NATURAL SIZE.

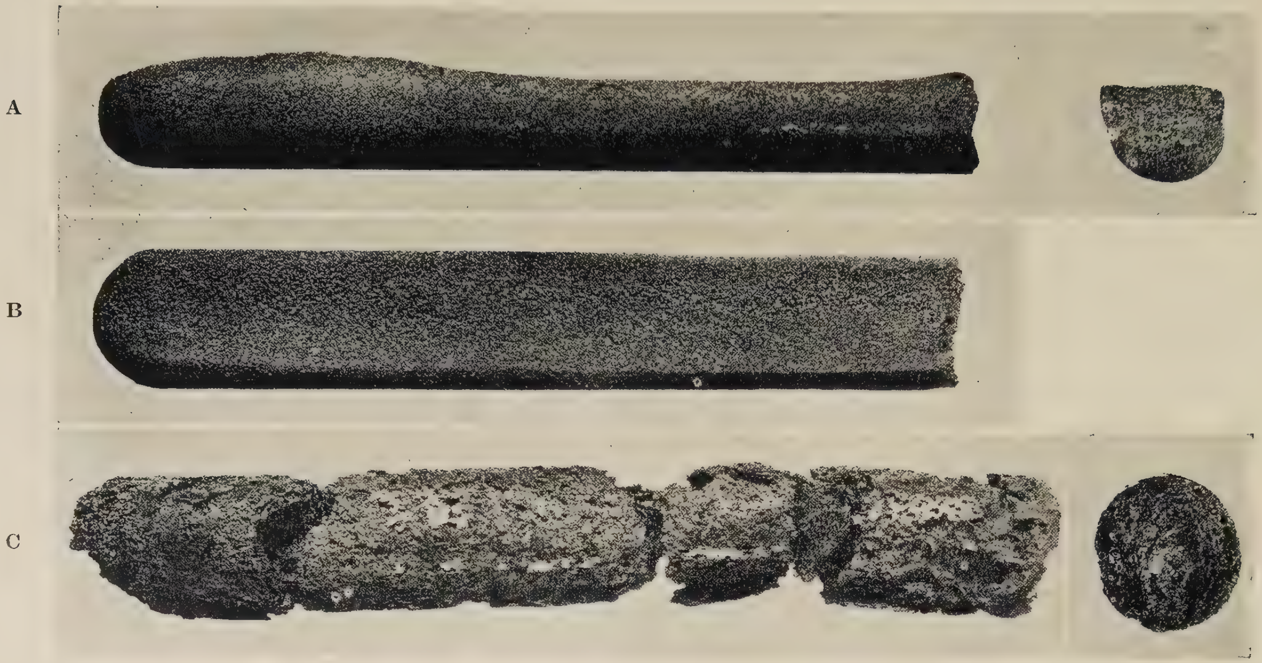

FIG. 40.

A and B. Dalton Main Coal—Produces a satisfactory Domestic Smokeless Fuel (Compare Fig. 32). C. Mitchell Main Coal, fusible coal, froths on carbonisation (Compare Fig. 30).

LABORATORY ASSAY COKES: SHOWING RESULTS OF BLENDING COALS OF WIDELY DIFFERING FUSIBILITY.

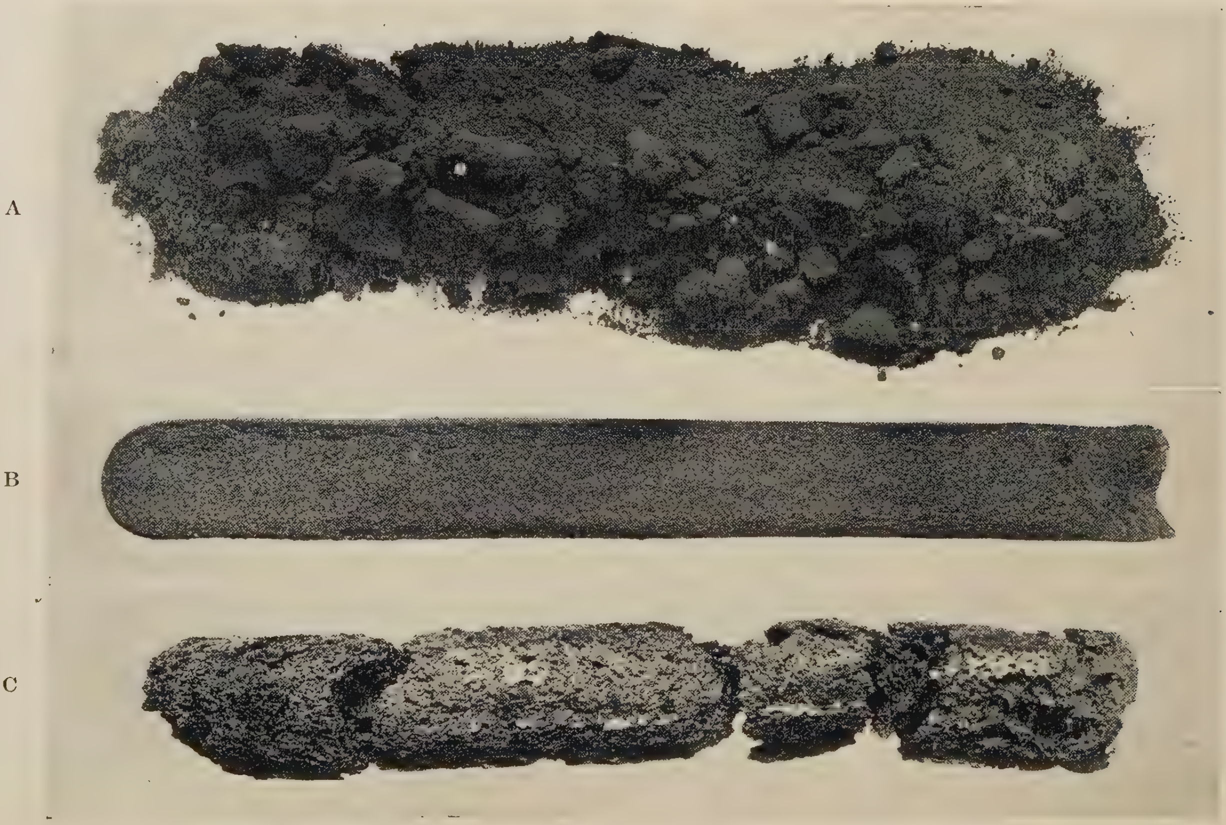

Fig. 41.

A. Non-Coherent Carbonaceous Residue from Ellistown Main Breeze. B. Open Spongy Coke from Mitchell Main Coal. C. Hard Shrunken Coke from a Blend of 40 per cent. Ellistown Main Coal and 60 per cent. Mitchell Main Coal.

LABORATORY ASSAY COKES FROM BLENDS OF MITCHELL MAIN COAL AND ELLISTOWN MAIN COAL.

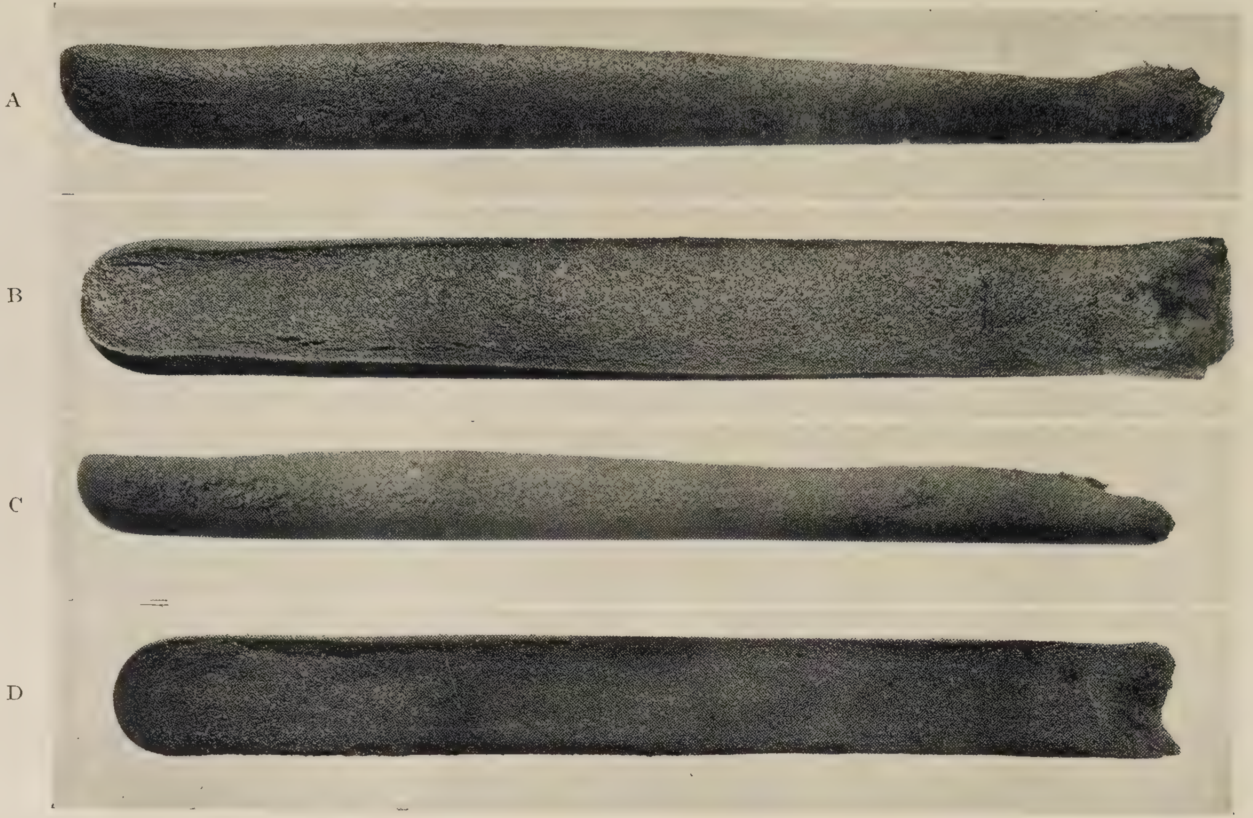

FIG. 42.

A and B. Elevation and Plan of Coke from Blend of 80 per cent. Mitchell Main Coal and 20 per cent. Ellistown Main Coal. C and D. Elevation and Plan of Coke from Blend of 60 per cent. Mitchell Main Coal and 40 per cent. Ellistown Main Coal. (Note greater shrinkage of 60-40 Blend.)

APPENDIX III

The Everard Davies Retort

The Everard Davies Retort is of the vertical type, and consists of two chambers placed on either side of a duct, through which the gases and tar evolved during carbonisation are withdrawn under suction to suitable recovery plant. The retort is designed to work at low or high temperatures, and by a sectional arrangement of the flues, zones of varying temperature can be maintained in the retort; thus the top zone of the retort may be maintained at 500° C., the central zone at 700° C., and the bottom zone at 900° C. Operating the retort for the production of low temperature carbonisation coke, the bottom zone is maintained at about 750° C., and the width of the charge lying between a heated surface and a withdrawal surface is from six to twelve inches at the top of the retort, tapering outwards slightly towards the bottom of the retort. Should the coal be briquetted prior to carbonisation this width may be increased to twenty-four inches. The retort works continuously or semi-continuously, the coal being fed into the retort from a hopper superimposed above the retort, and the coke passes from the retort through coke receiving chambers. The coke may be cooled by the admission of wet steam into the coke receiving chambers, or, provided a low temperature is maintained in the bottom zone, by quenching with water after the discharge from the retort. Mechanism is provided whereby superheated gases, such as waste gases and hydrogen, can be introduced into the retort either to obtain enhanced yields of gas and tar, or as a heating medium. It is stated that a solid compact fuel can be obtained from coal containing from 20 to 35 per cent. of volatile matter, and in the carbonisation of coals which do not give a coherent coke, briquetting of the coke, or carbonisation of the coal with a proportion of tar produced in a previous carbonisation, is advocated. By the withdrawal of the gas and tar under suction it is claimed that cracking is minimised and that swelling of the charge and consequent " sticking up " of the retort is avoided.

Complete Gasification of Coal with Tar Recovery in Special Types of Producers

The complete gasification of coal may be carried out to yield two distinct types of gas, (1) a gas of comparatively low calorific value—120 to 180 B.Th.U's. per c. ft.—such as producer gas,

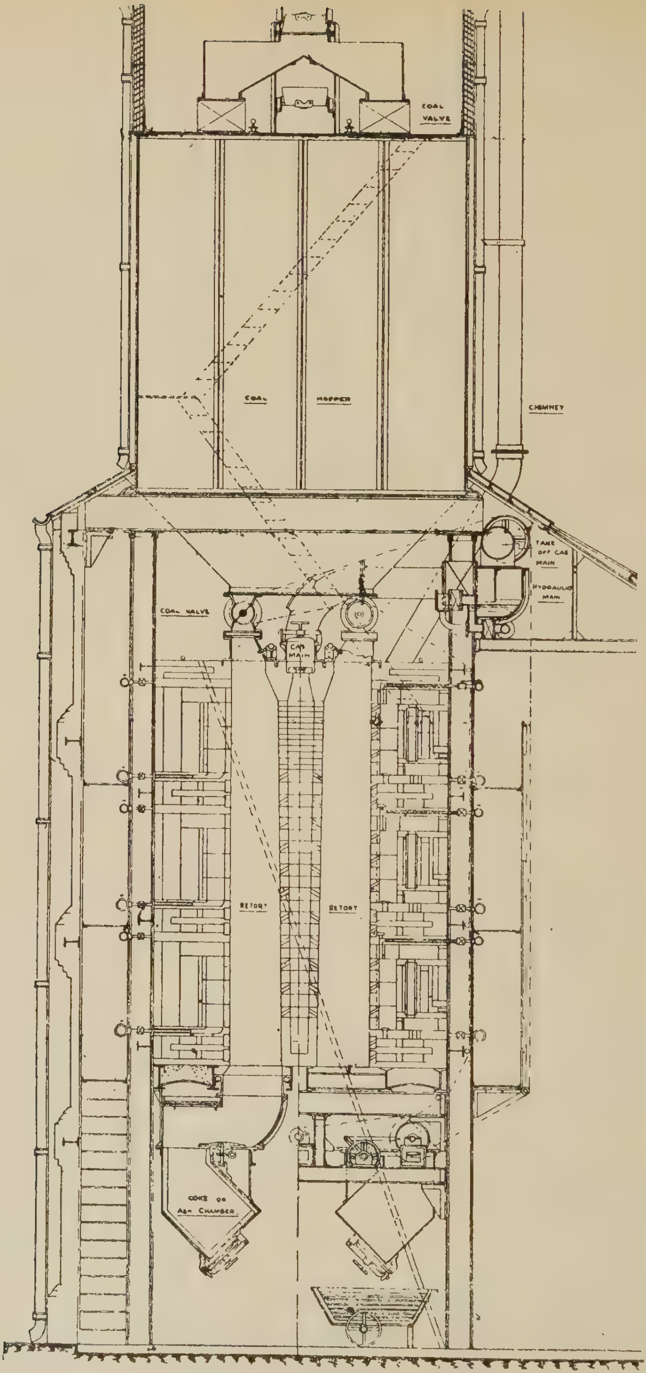

Fig. 43—Everard Davies Retort.

Mond gas or semi-water gas, and (2) a richer gas of calorific value 280 to 400 B.Th.U's. per c. ft.

The limits and adaptability of the ordinary producer plant to different types of fuel are well known and will not be discussed here. Particular interest, however, is attached to those producers which yield the latter type of gas. The objects in view in designing plant suitable for the purpose are (1) to effect the complete gasification of coal in a single stage, that is, to combine the processes of retorting and subsequent gasification in a producer, (2) to utilise, if desirable, a caking coal, (3) to obtain a gas of calorific value much higher than that of ordinary producer gas, and (4) to recover a low temperature tar.

To achieve these objects, the plants designed have taken the form of a producer surmounted by a retort, so arranged that the coal during its passage through the retort, is distilled at a low temperature by the gases from the producer proper. By this means, a low temperature tar is obtained, whilst the residual coke passes out of the retort and into the body of the producer where it is completely gasified. This procedure results in a yield per ton of coal treated of from 40,000 to 60,000 c. ft. of gas, varying in calorific value from 280 to 400 B.Th.U's. per c. ft., whilst from 8 to 20 gals. of low temperature tar may be recovered.

One of the first successful plants of this type was introduced by Strache in 1895 (German Patent 90,747, 1895), to manufacture what he termed "Doppelgas." His apparatus consists of a short vertical retort, superimposed upon a water gas producer, the latter being operated in the usual manner. During the "blow" period, the products pass round the outside of the retort, whilst in the subsequent "make" period, the gases sweep through the retort, thus removing the products of distillation.

Another plant yielding similar results is the "Trigas" generator of the Dellwik-Fleischer Water Gas Company. Owing to the construction of the plant and to the method of operation, a mixture of coal gas, water gas, and producer gas is obtained. Pott and Dolensky (J. für Gasbeleucht. 1919. 261) give the following figures relating to this plant. The coal employed consisted of a mixture of 75 per cent. bituminous coal and 25 per cent. brown coal. The gas yield amounted to 63,450 c. ft. per ton of coal, whilst the calorific value of the gas was 315-338 B.Th.U's. per c. ft. 5 to 6 per cent. of tar of the following composition was obtained:

	Percentage Composition
Lubricating oils	26·7
Highly viscous oils	32·5
Solid Paraffin	3·3
Resin	11·5
Pitch	26·0

Nature of tar—true low temperature tar, free from naphthalene.

Many different plants designed to effect complete gasification, and at the same time to yield a gas of high calorific value, are now on the market, but space will not permit a description of them here. The Tully Gas Plant, the Smith "Double-gas" Plant, the Doherty and the Drake plants are of the above type. An apparatus is now being built by the A.G. für Brennstoffvergasung for combining low temperature carbonisation with complete gasification and consists of a producer with a rotating top, to which is attached an annular iron retort extending downwards into the generator itself, the retort being heated partly by the passage of the producer gas through the retort, and partly by the hot gases passing round its outer surfaces. A similar type of producer is constructed by the Dutch Mondgas a. Nebenprodukten, Berlin.

READER'S NOTES

READER'S NOTES

BIBLIOGRAPHY

CHEMICAL SECTION

BEILBY, G. T.
The Destructive Distillation of Coal. Brit.Assoc. Sept. 1913. J. Gas Light. 1913. 123. 838.

BEILBY, G.
The Structure of Coke: Its Origin and Development. J.Soc.Chem.Ind. 1922. 41. 341T.

BENSON, H. K., and R. E. CANFIELD.
Low Temperature Distillation of Sub-Bituminous Coals. J.Ind.Eng.Chem. 1920. 12. 443.

BINDER.
Data on the Production of Soot by Different Coals. Wärme Kälte. Tech. 1922. Sept. 211.

BONE, W. A., A. R. PEARSON, E. SINKINSON and W. E. STOCKINGS.
The Resinic Constituents and Coking Propensities of Coal. Proc.Roy.Soc. 1922. A100. 582.

BORNSTEIN, E.
Pyrocatechol from Coal. Ber. 1902. 35. 4324.
The Decomposition of Solid Fuels at Gradually Increasing Temperatures. J. für Gasbeleucht. 1906. 49. 627. 648. and 667.

BROOKS, B. T., and J. HUMPHREY.
The Action of Concentrated Sulphuric Acid on Olefines with Particular Reference to the Refining of Petroleum Distillates. J.Amer.Chem.Soc. 1918. 40. 822.

BOUDOUARD, O.
The Coking Power of Coals. Comptes Rend. 1909. 148. 348. Rev.Mét. 1909. 6. 446.

BURGESS, M. J., and R. V. WHEELER.
The Volatile Constituents of Coal. Trans.Chem.Soc. 1910. 97. 1917; 1911. 99. 649.

The Distillation of Coal in a Vacuum. Trans.Chem. Soc. 1914. 105. 131.

CAMPBELL, A. F.
The Separation of m- and p-Cresols from Coal Tar Crude Carbolic Acid. J.Ind.Eng.Chem. 1922. 14. 732.

CHANEY, W.
Low Temperature Carbonisation and the Therm. Gas J. 1922. 159. 475; 160. 105, 367, and 492.

CLARK, A. H., and R. V. WHEELER.
The Volatile Constituents of Coal. Part III. Trans.Chem.Soc. 1913. 103. 1704.

COBB, J. W.
Nitrogen as Ammonia from Coal. J. Gas Light. 1914. 126. 329.
Thermal Phenomena in Carbonisation. J. Gas Light. 1914. 126. 917.

COHEN, J. B.
Report of the Committee on Smoke and Noxious Vapours Abatement. (H.M. Stationery Office) J.Soc.Chem.Ind. 1922. 41. 1R and 144R.

DAVIS, J. D., P. B. PLACE and G. S. SCOTT.
The Destructive Distillation of Mixtures of Oil and Coal. Chem.Met.Eng. 1921. 25. 1131.

DAVIS, J. D., and C. E. COLMAN.
The Low Temperature Distillation of Mixtures of Non-Caking Coals and Asphaltic Oils. Chem.Met. Eng. 1922. 26. 173.

DAWSON, H. M., and C. A. MOUNTFORD.
The Freezing Point of Mixtures of Phenol, o-Cresol, m-Cresol and p-Cresol. Trans.Chem.Soc. 1918. 113. 923.

DEMOULIN, G. E. J.
The Carbonisation of Coal at Low Temperatures. Chal.Ind. 1922. 1595.

DOLCH, M.
The Economy of Production of Low Temperature Tar. Zeit.angew.Chem. 1921. 34. 648.

DONATH, E.
THEORY OF THE COKING PROCESS. Stahl u. Eisen. 1914. 34. 60.

DRAKELEY, T. J., and F. W. SMITH.
THE ULTIMATE COMPOSITION OF BRITISH COALS. Trans. Chem.Soc. 1922. 121. 221.

EVANS, E. C.
ASPECTS OF LOW TEMPERATURE CARBONISATION OF COAL. J.Soc.Chem.Ind. 1918. 37, 212T.

EVANS, H. G.
THE ESTIMATION OF PARAFFINS AND UNSATURATED HYDROCARBONS IN COMMERCIAL TOLUOLS. J.Soc.Chem.Ind. 1919. 38. 402T.

EVANS, O.B.
THE CARBONISATION OF COAL IN VERTICAL RETORTS. J. Gas Light. 1913. 124. 587.

EVETTS, G.
LOW TEMPERATURE CARBONISATION AND THE ECONOMICS OF MANUFACTURE. Gas J. 1922. 160. 427.

FINDLEY, A. E., and R. WIGGINTON.
THE SEPARATION OF THE CONSTITUENTS OF BANDED BITUMINOUS COAL. Fuel. June. 1922. 106.

FISCHER, F.
COAL AS A SOURCE OF NEW CHEMICAL RAW MATERIALS. Brennstoff Chem. 1920. 1. 31 and 47.
THE PRODUCTION OF MOTOR SPIRIT FROM LOW TEMPERATURE TARS, FROM COAL AND LIGNITE, AND THE CONVERSION OF THE PHENOLS OR CREOSOTE INTO BENZOL. Brennstoff Chem. 1921. 2. 327 and 347.

FISCHER, F., and W. GLUUD.
GES ABHANDL. ZUR KENNTNIS DER KOHLE, VOLS. I-IV. 1916-1918.
A NEW PRACTICAL METHOD OF LOW TEMPERATURE CARBONISATION. Ber. 1919. 52. 1035.

FISCHER, F., and H. SCHRADER.
NEW CONTRIBUTION ON THE ORIGIN AND CHEMICAL STRUCTURE OF COAL. Fuel. July. 1922. 113.

FISCHER, F., H. SCHRADER and C. ZERBE.
The Absence of Naphthalene and the Presence of its Derivatives in Low Temperature Tar. Brennstoff Chem. 1922. 3. 57.

FISHENDEN, M. W.
The Efficiency of Low Temperature Coke in Domestic Appliances. Fuel Research Board. Dept. of Scientific and Industrial Research. Tech. Paper No. 3. H.M. Stationery Office. 1921.

FOERSTER, F.
Behaviour of the Sulphur in Coal During Dry Distillation. Zeit.angew.Chem. 1922. 35. 343.

FOERSTER, F., and W. GEISLER.
The Behaviour of Sulphur in Coal in Dry Distillation. Zeit.angew.Chem. 1922. 35. 193.

FOX, J. J., and M. F. BARKER.
The Determination of Phenol in Commercial Cresylic Acid. J.Soc.Chem.Ind. 1917. 36. 842.
The Estimation of Phenol in Cresylic Acid. J.Soc. Chem.Ind. 1918. 37. 265T.
The Solidifying and Boiling Points of Phenol and the Cresols. J.Soc.Chem.Ind. 1918. 37. 268T.
The Analysis and Composition of Cresylic Acid. J.Soc.Chem.Ind. 1920. 39. 169T.

FOXWELL, G. E.
The Thermal Dissociation of Ammonia. J.Soc.Chem. Ind. 1922. 61. 114T.

GREENWOOD, H. D., and J. W. COBB.
The Structure of Coke. J.Soc.Chem.Ind. 1922. 41. 181T.

HARGER, J.
Coal and the Chemistry of its Carbonisation. J.Soc.Chem.Ind. 1915. 33. 389.

HOLLINGS, H., and J. W. COBB.
A Thermal Study of the Carbonisation Process. Trans.Chem.Soc. 1915. 107. 1106.

HULETT, G. A., and J. H. CAPPS.
The Distillation of Coal under Pressure. J.Ind.Eng. Chem. 1917. 9. 927.

ILLINGWORTH, S. R.

Coal and its Carbonisation. Fuel. Jan. 1922. 49.

Researches on Coal. Part I. The Thermal Decomposition of Coal at Low Temperatures. J.Soc.Chem.Ind. 1920. 39. 111T.

Researches on Coal. Part II. An Investigation of Certain Coking Coals. A Theory of Coking. J.Soc.Chem.Ind. 1920. 39. 133T.

INGRAM, J. C.

Oils and Tars from Bituminous Materials. School of Mines. Univ. of Missouri. Bull. No. 4. 1917.

JONES, D. T.

The Thermal Decomposition of Low Temperature Tar. J.Soc.Chem.Ind. 1917. 36. 3.

JONES, D. T., and R. V. WHEELER.

The Composition of Coal. Part I. Trans.Chem.Soc. 1914. 105. 140.

The Composition of Coal. Part II. Trans.Chem.Soc. 1914. 105. 2562.

The Composition of Coal. Part III. Trans.Chem.Soc. 1915. 107. 1318.

The Constitution of Coal. Trans.Chem.Soc. 1916, 109. 707.

KNIGHT, G. W., C. T. LINCOLN, G. FORMANEK, and H. L. FOLLETT.

The Estimation of Phenol in the Presence of the Three Cresols. J.Ind.Eng.Chem. 1918. 10. 9.

LANDER, C. H., and others.

Low Temperature Carbonisation of Coal. Proc. S. Wales Inst. Eng. 1922. 38. 2. 122.

LANT, R.

The Determination of the Degree of Swelling in Coking. Brennstoff Chem. 1922. 3. 97.

LESSING, R.

The Behaviour of the Constituents of Banded Bituminous Coals on Coking. Trans.Chem.Soc. 1920. 117. 247.

The Carbonisation of Coal. Fuel. August. 1922. 137.

LEWES, V. B.

The Carbonisation of Coal. J.Roy.Soc.Arts. 1911. 60. 135.

LIERG, F.
Contribution to the Chemistry of the Coking Process—The Use of Refractory Bitumen in the Production of Metallurgical Coke from Non-caking Coals. Zeit.angew.Chem. 1922. 35. 264.

MACLAURIN, R.
Low Temperature Carbonisation. J.Soc.Chem.Ind. 1917. 36. 620.

M'LEOD, J.
Distribution of Nitrogen in the Distillation of Coal. J.Soc.Chem.Ind. 1907. 26. 136.

MAHLER, P., and E. CHERON.
Distillation of Coal. Comptes Rend. 1910. 150. 1604.

MARCUSSON, J., and M. PICARD.
The Composition of High and Low Temperature Tar. Zeit.angew.Chem. 1921. 34. 201; 1922. 35. 493.

MARSHALL, F. D.
Low Temperature Carbonisation. Gas J. 1918. 142. 381.
Low Temperature Carbonisation and Oil Production. Gas J. 1918. 142. 236.

MAYER, M., and V. ALTMEYER.
The Production of Ammonia during the Dry Distillation of Coal. J.für.Gasbeleucht. March. 1907. J. Gas Light. 1907. 98. 27. and 157.

MONKHOUSE, A. C., and J. W. COBB.
The Liberation of Nitrogen from Coal and Coke as Ammonia. Gas J. 1921. 156. 231.

MOORE, H.
Fuel Oils from Coal. Manch.Ass.Eng. Feb. 1916.

MORGAN, J. J., and R. P. SOULE.
Studies in the Carbonisation of Coal. Characteristics of Low Temperature Coal Tar. Chem.Met.Eng. 1922. 26. 923. and 977.

PARR, S. W., and C. K. FRANCES.
The Modifications of Illinois Coal by Low Temperature Distillation. Bull. 24. 1912. Eng. Expt. Stat. Univ. of Illinois.

PARR, S. W., and T. E. LAYNG.
Low Temperature Carbonisation and its Application to High Oxygen Coals. J.Ind.Eng.Chem. 1921. 13. 14.

PARR, S. W., and H. S. OLIN.
The Coking of Coal at Low Temperatures and a Preliminary Study of the By-Products. Bull. 60. 1912. Eng. Expt. Stat. Univ. of Illinois.
The Coking of Coal at Low Temperatures with Special Reference to the Properties and Composition of the Products. Bull. 79. 1915. Eng. Expt. Stat. Univ. of Illinois.
The Coking of Coal at Low Temperatures. Scient. Amer.Suppl. 1913. 252.

PETERS, F.
On the Uses of Low Temperature Tar for the Preservation of Wood. Brennstoff Chem. 1922. 3. 198.

PICTET, A.
Researches on Coal. Ann.Chim. 1918. 9. 10. 249.

PICTET, A., and M. BOUVIER.
Distillation of Coal under Reduced Pressure. Comptes rend. 1913. 157. 779. Ber. 1913. 46. 3342.
Vacuum Tar. Chem.Zeit. 1914. 38. 10. Comptes rend. 1913. 157. 1436. Comptes rend. 1915. 160. 629.
The Saturated Hydrocarbons of Vacuum Tar. Ber. 1915. 48. 926.

PICTET, A., O. KAISER, and LABOUCHÈRE.
Vacuum Tar. Comptes rend. 1917. 165. 113. and 358.

PICTET, A., and L. RAMSEYER.
Hexahydrofluorene in Coal. Chem.Zeit. 1911. 35. 865.

PICTET, A., O. KAISER, and L. RAMSEYER.
Hydrocarbons in Coal. Comptes rend. 1916. 163. 358.

PLATT, C. B., and R. V. WHEELER.
The Volatile Constituents of Coal. Part III. Addendum. Trans.Chem.Soc. 1913. 103. 1713.

PORTER, H. C., and F. K. OVITZ.
Nature of Volatile Matter of Coal Evolved under Different Conditions. J. Gas Light. 1908. 104. 343.
The Volatile Matter of Coal. Bull. 1. 1912. U.S. Bureau of Mines.

PORTER, H. C., and G. B. TAYLOR.
The Mode of Decomposition of Coal by Heat. Amer. Gas.Inst. 9th. Ann.Meet.Chem.Sect. 1914. 1.

RASCHIG, F.
The Behaviour of m-Cresol in Mixtures of the Cresols. Zeit.angew.Chem. 1900. 14. 759.

ROBERTS, J.
The Carbonisation of Coal at Low Temperatures. Trans.Inst.Min.Eng. 1921. 62. 9.

SHORT, A.
Distribution of Nitrogen and Sulphur in the Carbonisation of Durham Coking Coal. J.Soc.Chem.Ind. 1907. 26. 581.

SIMMERSBACH, O.
The Formation of Ammonia and Cyanogen in Carbonisation. J. Gas Light. 1915. 131. 246.

SINNATT, F. S., and A. GROUNDS.
A New Characteristic for Coal: The Agglutinating Power Curve. J.Soc.Chem.Ind. 1920. 39. 83T.

STOPES, M. C.
Remarks on Vitrain. Fuel. Feb. 1922. 22.
The Constitution of Coal. Fuel. June. 1922. 93.
The Four Visible Ingredients in Banded Bituminous Coals. Proc.Roy.Soc. 1919. B. 90. 470.

SUTCLIFFE, E. R., and E. C. EVANS.
Low Versus High Temperature Carbonisation for the Production of Smokeless Fuel. Proc.S.Wales.Inst. Eng. Gas J. 1922. 158. 631.
The Influence of Structure on the Combustibility and Other Properties of Solid Fuels. J.Soc.Chem. Ind. 1922. 41. 196T.

TERRES, E.
The Condition of Nitrogen in Coal and Coke. J. Gasbeleucht. 1916. 59. 519.

THAU, A.
On the Low Temperature Carbonisation of Coal. Bergb. 1922. 949 and 993.

THOLE, F. B.
The Estimation of Benzene and Toluene in Petroleum. J.Soc.Chem.Ind. 1919. 38. 39T.

TIDESWELL, F. V., and R. V. WHEELER.
Oxidation of the Ingredients of Banded Bituminous Coal. Trans.Chem.Soc. 1920. 117. 794.

TROPSCH, H.
The Composition of High and Low Temperature Tar. Brennstoff Chem. 1921. 2. 251.
Note on Vacuum Tar from Gas Coal. Brennstoff Chem. 1921. 2. 312.

VIGNON, L.
The Fractional Distillation of Coal. Comptes rend. 1912. 155. 1514.

WEIGHELL, A.
The Agglutinating Value of Some Durham Coals. J.Soc.Chem.Ind. 1922. 41. 17T.

WEINDEL, A.
A Contribution to the Knowledge of the Primary Tar Phenols. Brennstoff Chem. 1922. 3. 245.

WEISS, J. M., and C. R. DOWNS.
The Determination of Phenol in Crude Carbolic Acid, and Tar Oils. J.Ind.Eng.Chem. 1917. 9. 569.

WEYMAN, G.
The Rate of Carbonisation of Coal. J.Soc.Chem.Ind. 1921. 40. 300T.

WHITAKER, M. C., and W. R. CROWELL.
Coal Carbonisation at Atmospheric Pressure. J.Ind. Eng.Chem. 1917. 9. 261.

WHITAKER, M. C., and J. R. SUYDAM.
The Nature of Tar. J.Ind.Eng.Chem. 1918. 10. 431.

WHITE, A. H., F. E. PARK, and W. A. DUNKLEY.
Destructive Distillation of Coal at Low Temperatures. J. Gas Light. 1908. 104. 348.

WIBAUT, J. P.
Sulphur Compounds in Coal and Coke. Brennstoff Chem. 1922. 3. 273.

WIGGINTON, R., and R. V. WHEELER.
The Resins in Bituminous Coals. Fuel. Jan. 1922. 10.

WINMILL, T. F.
The Low Temperature Distillation of Inferior Coals. J.Soc.Chem.Ind. 1917. 36. 912.

As general works of reference, the following books may be consulted:—

Coal and its Scientific Uses. W. A. Bone. Longmans Green & Co. (1918).

The Carbonisation of Coal. V. B. Lewes. Benn Bros. Ltd. (1918).

Coal Tar Distillation. A. R. Warnes. Benn Bros. Ltd. (1917).

The Manufacture of Sulphate of Ammonia and Crude Ammonia. G. T. Calvert. Benn Bros. Ltd.

Coal Tar and Ammonia. G. Lunge. Gurney and Jackson. (1909).

Reports of the Fuel Research Board. Dept. of Scientific and Industrial Research. H.M. Stationery Office.

The Report of the Committee on Smoke and Noxious Vapours Abatement. H.M. Stationery Office (1921).

The Constitution of Coal. M. C. Stopes and R. V. Wheeler. Dept. of Scientific and Industrial Research. H.M. Stationery Office (1918).

A Treatise on British Fuel Oil. J. A. Greene. Griffin & Co. Ltd. (1919).

Nitrogen Products Committee Final Report. H.M. Stationery Office (1920).

The Smokeless City. E. D. Simon and M. Fitzgerald. Longmans Green & Co. (1922).

Smoke. A Study of Town Air. J. B. Cohen and A. G. Ruston. Edward Arnold (1912).

Industrial Uses of Fuel Oil. F. B. Dunn. Technical Publishing Co. San Francisco. Spon London (1916).

The Fuel Economy Report. British Association (1922).

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